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ON THE DECOMPOSITION OF DIAZO COMPOUNDS.

X.—A STUDY OF THE ACTION OF THE NITRATE AND SULPHATE OF PARADIAZOTOLUENE ON METHYL ALCOHOL UNDER VARIOUS CONDITIONS.[1]

BY WILLIAM E. CHAMBERLAIN.

The following pages contain an account of the action of paradiazotoluene nitrate and sulphate on methyl alcohol under various conditions of temperature and pressure, together with a study of the effect of sodium methylate, caustic potash, potassium carbonate, zinc dust, and zinc oxide on the course of the reaction.

Decomposition of Paradiazotoluene Nitrate with Methyl Alcohol at the Ordinary Atmospheric Pressure.

40 grams of paradiazotoluene nitrate were placed in a long-necked balloon flask of one liter capacity and covered with 100 cc. absolute methyl alcohol (from lime); the flask was then put into a water-bath and provided with a return-condenser. The decomposition began at the room temperature, but was very slow. On heating the water-bath to 55° C., the decomposition went on quietly and rapidly. When bubbles of nitrogen had ceased to appear, the alcohol was boiled for a short time to insure complete decomposition. In this way

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[1] From the Author's Thesis submitted to the Board of University Studies of the Johns Hopkins University for the degree of Doctor of Philosophy, June, 1894.

133 grams of diazo compound were decomposed with about 450 cc. absolute methyl alcohol.

The different portions were united and the alcohol boiled off. The alcoholic distillate was poured into five times its bulk of a saturated solution of sodium chloride. A yellow oil rose to the surface and was separated. The residue in the flask was made alkaline and distilled with steam, when a further quantity of yellow oil passed over. This was united with the oil from the alcoholic distillate, washed with caustic soda, then several times with water, dried with calcium chloride, and fractionated. A few drops came over between 100° and 130°, the main portion at 172°–177°, and about 2 cc. above 180°.

The lower-boiling fraction was tested for toluene by treatment with fuming nitric acid, and a liquid was obtained which had the odor of nitrobenzene. This was reduced in a test-tube with tin and hydrochloric acid, the whole made alkaline, and distilled with steam. An oil came over which had the odor of paratoluidine, but the quantity was too small for satisfactory testing.

The fraction boiling between 172° and 177° was redistilled several times, when it boiled at 174°.5 (cor.). 18 grams of a colorless, mobile oil were thus obtained. Its boiling-point corresponds to that of the methyl ether of paracresol (174°–175°) described by Körner.[1] To test further its identity, 2 grams of the oil were oxidized with potassium permanganate in alkaline solution, and an acid obtained which melted at 184° (cor.). This agreed fairly well with the melting-point given for anisic acid (185°). The oil is therefore the methyl ether of paracresol, $CH_3.C_6H_4.OCH_3(p)$.

The fraction of the oil which came over above 180° was found to have no definite boiling-point, and was probably a complex mixture. Nothing was done with it.

The residue in the steam-flask was acidified with sulphuric acid and again distilled with steam. Nothing came over except water.

The contents of the steam-flask were poured out and the liquid evaporated. Nothing was found but sodium sulphate.

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[1] Ztschr. Chem., 1868, 326.

The tar—a black, solid mass—was extracted with petroleum ether (boiling-boint 80°) after several other solvents had been tried, and 3 grams of a yellow solid obtained, which, on recrystallizing several times from petroleum ether and from alcohol, melted at 80°.5 (cor.). The crystals obtained from petroleum ether were long, flat needles with serrated edges. These were not brittle, and were consequently difficult to powder. The crystals obtained from alcohol were fine, sharp needles which were quite brittle.

The melting-point and other physical properties of this substance made it probable that it was identical with the dinitroparacresol (melting-point 85°) obtained by Städel by action of nitric acid upon the ethyl ether of paracresol.[1] To prove its identity the potassium salt was made, from it the silver salt, and from this, by treatment with ethyl iodide in a pressure-bottle, the ethyl ether. This substance agreed with the description given by Städel of the ethyl ether of paracresol. The melting-point found was 71°; that given by Städel is 75°.

The relative difference between the melting-points of the dinitrocresol and of its ethyl ether, as found by Städel and myself, is the same. I judge, therefore, that the difference is due to the thermometers. The thermometer used throughout this investigation was carefully compared with a standard thermometer for temperatures between 14° and 92°. Temperatures near 183° were corrected by the boiling-point of aniline.

The melting-point of dinitroparacresol (CH_3, NO_2, OH, $NO_2 = 1, 3, 4, 5$) is given by different investigators variously as 79°, 80°,[2] 82°,[3] 83°,[4] 83°.5,[5] 84°,[6] 85°.[7] To test the melting-point with more accuracy, a quantity of dinitrocresol was prepared. 36 grams of paracresol were diluted with 36 grams glacial acetic acid. 54 grams nitric acid (sp. gr. 1.4) were diluted with 108 grams glacial acetic acid. The two solutions were dropped slowly from dropping-funnels into a flask surrounded by a freezing-mixture. After several hours the

[1] Ann. Chem. (Liebig), **217**, 163.

[2] Ber. d. chem. Ges , **13**, 1946.

[3] *Ibid*, **6**, 974.

[4] *Ibid*, **7**, 1023; **14**, 568.

[5] *Ibid*, **7**, 536.

[6] *Ibid*, **2**, 207 : **8**, 685 ; **14**, 986 ; Ann. Chem. (Liebig), **173**, 205.

[7] Jsb., 1866, p. 360.

mixture was warmed on a water-bath and poured into much cold water. A yellow solid separated out. It was distilled with steam to free it from the more volatile mononitrocresol. The residue in the steam-flask, consisting wholly of dinitroparacresol, was recrystallized from alcohol until repeated recrystallization failed to make any change in the melting-point. The melting-point of the dinitroparacresol was found to be constant at 80°.5 (cor.).

Action of Nitric Acid on Paramethoxytoluene.

In view of the fact already mentioned, that Städel obtained dinitroparacresol from paraethoxytoluene by action of nitric acid, it was thought that the action of nitric acid, both dilute and concentrated, upon paramethoxytoluene would also prove of interest. 10 grams of paramethoxytoluene and 20 grams pure nitric acid (sp. gr. 1.4) were each diluted with 20 grams glacial acetic acid. The two solutions were dropped slowly into a flask surrounded with ice and allowed to stand over night. In the morning the solution was poured into much cold water and the whole allowed to stand. The next day the water had cleared up, and at the bottom was an oil which was full of crystals. These were separated from the oil by the filter-pump, and recrystallized from alcohol. They melted at 80°.5. This showed them to be dinitroparacresol. To establish the identity of this substance, the ethyl ether was made as before. It melted at 71°.

The quantity of oil from which the crystals were separated was so small that nothing more was done with it. Some work done later makes it probable that it was mononitrocresol.

10 grams of paramethoxytoluene were poured slowly from a dropping-funnel on to 40 grams pure concentrated nitric acid, in a flask provided with a return-condenser. Heat was applied to start the reaction. Abundant red fumes were given off. After some time the reaction became somewhat less violent, and 20 grams of fuming nitric acid were added and the rest of the ether was run in. 10 grams of concentrated nitric acid and 20 grams of concentrated sulphuric acid were then added and the mixture boiled until the red fumes

ceased to appear. The whole was then poured into cold water, and after a time the oil which first separated out became partially solid. The crystals were separated from the oil by the filter-pump, and recrystallized from alcohol. They melted at 122°. The crystals were needles of a slightly yellowish color. They looked like the ethyl ether of dinitroparacresol. The melting-point showed them to be the methyl ether of dinitroparacresol. The yield was very small, only 0.2 gram of purified substance. Most of the ether had been oxidized completely by the strong nitric acid.

The action of dilute nitric acid upon paramethoxytoluene is, thus, not only to introduce the nitro groups, but also to saponify the ether. This is what one would expect from the work of Städel. From paracresol ethyl ether he obtained dinitroparacresol and dinitroparacresol ethyl ether[1]; from orthocresol ethyl ether he obtained almost exclusively dinitroorthocresol[2]; from paracresol benzoyl ether, dinitroparacresol.[3] This reaction of dilute nitric acid is somewhat surprising. Saponification does not usually result from such mild treatment. Some of the dinitrocresol ethyl ether was boiled with moderately dilute nitric acid for several hours without any effect whatever. It is probable that, when the nitro groups are entering, the equilibrium of the molecule is so disturbed that saponification is effected by means which do not ordinarily produce that result.

Another experiment was made with 205 grams of paradiazotoluene nitrate, in the hope of determining more accurately the character of the reaction with methyl alcohol, both as to the yield of ether and also as to the other substances formed. The decomposition and study of the products were carried on as before described. The oil separated into three fractions: one, about 1 cc., boiling at 100°–130°; the main portion, about 40 grams, boiling at 173°–177°, most of it at 175°; and about 2 cc., boiling at 215°–225°. There was some tar left in the bulb at 260°.

The fraction boiling at 100°–130°, supposed to be toluene, was boiled with strong nitric and sulphuric acids until action ceased, and then the whole was poured on ice. A white solid separated out, which was recrystallized from alcohol and found to melt at 70°.5. This is ordinary dinitrotoluene (2, 4), and proves the presence of toluene among the decomposition-products of the diazo compound.

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[1] Ann. Chem. (Liebig), **217**, 161.

[2] *Ibid*, **217**, 168.

[3] *Ibid*, **217**, 180.

The fraction boiling at 215°–225° (only about 2 cc.) was oxidized with potassium permanganate, in the hope that a crystalline substance might be obtained which would identify it. A few white crystals looking something like urea were obtained, which melted at 181° (cor.), but the quantity was too small to permit of an analysis.

The tarry residue in the steam-flask was extracted with petroleum ether, as before, and 5.5 grams of dinitroparacresol obtained, melting at 80°.5. The residues and distillates were thoroughly worked over, but nothing further was found in them.

The main product of the reaction between methyl alcohol and paradiazotoluene nitrate at the ordinary atmospheric pressure is paramethoxytoluene. A very small quantity of toluene is also formed, due, probably, to the action of the nitric acid liberated in the reaction. The reaction thus consists mainly in the substitution of the methoxyl for the diazo group :

$$CH_3.C_6H_4.N_2.NO_3 + CH_3OH = CH_3.C_6H_4.OCH_3 + HNO_3 + N_2.$$

The presence of toluene is accounted for by the reaction :

$$CH_3.C_6H_4.N_2.NO_3 + CH_3OH = C_6H_5.CH_3 + CH_2O + HNO_3 + N_2.$$

There was no odor of formaldehyde perceived during the decomposition, and no indication of the presence of formaldehyde or if its polymers was found among the products of decomposition.

Decomposition of Paradiazotoluene Sulphate with Methyl Alcohol at the Ordinary Atmospheric Pressure.

47 grams of paradiazotoluene sulphate were placed in a flask provided with a return-condenser, together with 200 cc.

absolute methyl alcohol, and the flask placed in a water-bath. The decomposition did not begin until the boiling-point of the alcohol was reached. The evolution of nitrogen went on quietly and steadily, and in about half an hour the decomposition was complete.

60 grams of diazotoluene sulphate were decomposed, in the same way, with 250 cc. absolute methyl alcohol.

The two portions were united and the alcohol boiled off. The distillate was treated with salt solution and a yellow oil separated. The distillation was then continued with steam, and the yellow oil which came over separated and united with that from the alcoholic distillate. The yield of crude oil was 40 grams. On fractionating, almost all of the oil came over at 170°–180°, and, on redistilling, at 174°–176° (cor.). This is, again, the methyl ether of paracresol.

A few drops of oil distilled over below 170°, and when redistilled, 5 or 6 drops came over at 100°–130°. These were treated with strong nitric and sulphuric acids, and crystals obtained melting at 70°, proving the presence of a minute quantity of toluene among the decomposition-products.

A small quantity of yellow oil distilled above 180°. An unsuccessful attempt was made to get crystals from it. The quantity of tar left in the steam-flask was very small, compared with that obtained in the decomposition of the diazo nitrate.

Part of the liquid in the steam-flask was neutralized with barium carbonate and filtered. Addition of sulphuric acid to the filtrate produced a slight cloudiness, probably due to the presence of a sulphonic acid, as any methylsulphuric acid, if formed, would have been decomposed by the steam.

The reaction with the diazo sulphate is, again, the methoxy reaction, almost exclusively. The reaction is much cleaner than is the case with the nitrate, and the yield of methoxytoluene is much larger.

Decomposition of Paradiazotoluene Nitrate with Methyl Alcohol under Diminished Pressure.

In this experiment, 41 grams of paradiazotoluene nitrate were decomposed with 120 cc. of absolute methyl alcohol.

The flask was connected with a return-condenser, the upper end of which was joined to a suction-pump and a manometer. During the experiment the manometer showed a depression of 490–500 mm. Slight signs of decomposition were observed at the ordinary temperature. At 40° the decomposition went on steadily. The escaping gases were passed through water, and the water was tested for an aldehyde with ammoniacal silver nitrate, but no indication of an aldehyde was found.

The products were studied as above described, first boiling off the alcohol, then making the contents of the flask alkaline, and distilling with steam. The yellow oil which came over separated, when distilled, into two fractions, one boiling at 105°–112°, and the other at 172°–177°, showing that here, again, toluene and methoxytoluene were the products of decomposition. The yield was better than in the experiment with the nitrate at ordinary pressure—6 cc. of ether and 2 of toluene. There was a small quantity of oil left in the distilling bulb at 180°. This was found to contain toluidine which had not been diazotized.

When the distillate from the steam-flask came over clear, the contents of the flask were acidified and steam again passed through. About 2 cc. of a dark-red oil distilled over, which solidified when placed in a freezing-mixture. The mass was put on a drying-plate and the crystals dissolved in alcohol. On cooling the alcohol they reappeared, and were separated and dried (melting-point 32°). The substance looked and smelled like orthonitrophenol. Treated with caustic soda its solution turned red. It was very soluble in alcohol and was volatile with boiling alcohol. These properties show that it is the mononitro derivative of paracresol (CH_3, NO_2, $OH = 1, 3, 4$).

The differences noted between this reaction and the one at ordinary pressure were such as were to be expected. The reaction was cleaner than the one at ordinary pressure, probably due to the lower temperature, and the nitro compound formed did not contain two nitro groups. It is to be noted, also, that the proportion of toluene was greater than in the reaction at ordinary pressure.

Decomposition of Paradiazotoluene Sulphate with Methyl Alcohol under Diminished Pressure.

Using the same method as in the preceding experiment, 57 grams of paradiazotoluene sulphate were decomposed with 250 cc. of absolute methyl alcohol, with a diminution from the ordinary pressure of 500 mm. The decomposition took place slowly when the methyl alcohol was heated up to its boiling-point, and was complete in about four hours. The alcohol was distilled off, the residue distilled with steam, and the oil from the different portions united. The yield of crude oil was 25 grams. On fractioning, a few drops came over between 100° and 120°, showing a slight trace of toluene. Almost the whole of the oil passed over between 172° and 177°. Only a very small quantity of tar was formed.

The reaction in this case is a very clean one. Methoxytoluene is the main product, with only a slight trace of toluene.

Decomposition of Paradiazotoluene Nitrate with Methyl Alcohol under Increased Pressure.

The experiments in which increased pressure was used were carried on in a balloon flask surrounded with wire netting. The flask was fitted with a 2-hole rubber stopper, and connection was made with a safety-valve and a manometer. By changing the weight on the safety-valve the pressure could be kept at any desired point.

In this way 46 grams of paradiazotoluene nitrate were decomposed with 200 cc. of absolute methyl alcohol, with an increase over the ordinary atmospheric pressure of 500 mm. Heat was applied, and the decomposition went on slowly and steadily at about 35°.

After the decomposition was finished the alcohol was distilled off under reduced pressure. On adding salt solution to the distillate only a very small quantity of oil separated. The contents of the flask were then made alkaline and distilled with steam. At first the distillate consisted only of water and oil. Soon, however, a very small quantity of orange-colored solid appeared in the condenser. The distillation with steam was continued till the distillate became clear, when the contents of the steam-flask were made acid with sulphuric acid, and the distillation with steam continued. A reddish oil now distilled over, which solidified in the receiver. The residue of tar was smaller than was the case when the decomposition took place at the ordinary pressure.

On fractionating the oil, no trace of toluene was found. Most of the oil—12 grams—passed over between 172° and 177°. A small quantity was left in the distilling bulb above 180°. This was poured into a small beaker and cooled in a freezing-mixture, when crystals appeared in it. These were filtered off and recrystallized from alcohol. They melted at 112°, and had the other properties of mononitrotoluidine. Their formation here was due to the action of the nitric acid upon a little undiazotized toluidine. About half a gram of this substance was obtained. This is the same as the red solid which distilled over from the alkaline solution.

The solid which distilled over from the acid solution was recrystallized from alcohol and found to melt at 32°. It was identical with the mononitrocresol obtained when working at reduced pressure. The yield was only 1.1 grams. Nothing crystallizable could be extracted from the tar.

The occurrence of mononitrocresol instead of dinitrocresol in this experiment is due, probably, to the fact that the alcohol was boiled off under reduced pressure, and the action of the nitric acid on the cresol ether was therefore not so energetic as when the alcohol was boiled off at a higher temperature.

Decomposition of Paradiazotoluene Sulphate with Methyl Alcohol under Increased Pressure.

In this experiment 66 grams of paradiazotoluene sulphate were decomposed with 200 cc. of absolute methyl alcohol under an increase of 550 mm. over the ordinary atmospheric pressure. The decomposition began at about 60°. The alcohol was boiled off and steam passed through the residue, exactly as in the case of the nitrate, except that the contents of the flask were not made alkaline. Yield of crude oil, 25 grams. On fractionating, a few drops came over below 140°, and were proved to contain toluene by making the dinitro derivative and testing the melting-point. Almost all of the oil distilled at 172°–177°. About 1 cc. of dark-red oil remained above 180°. This would not crystallize, and nothing was done with it. There was less tar formed in this reaction than in any other so far performed.

Here, again, the reaction consists almost entirely in the introduction of the methoxyl group.

Decomposition of Paradiazotoluene Nitrate with Sodium Methylate.

The work of Beeson[1] on the action of the diazobenzene nitrate and sulphate with sodium methylate, and with methyl alcohol in the presence of caustic potash and of zinc dust, made it probable that paradiazotoluene nitrate and sulphate would give the hydrogen reaction in the presence of these and similar substances.

44 grams of paradiazotoluene nitrate were added gradually to 200 cc. methyl alcohol in which 15 grams of sodium had been dissolved. The decomposition took place at once, with separation of sodium nitrate. The flask was kept in ice-water during the decomposition. The products of the decomposition were distilled with steam. 9 grams of crude oil were obtained. This proved to be toluene. Only a few drops of dark-red liquid remained in the distilling-bulb above 120°. This was probably tar carried over mechanically by the steam and dissolved by the toluene. There was a considerable quantity of dark-brown tar left in the steam flask. This showed minute crystals scattered through it, but all attempts to separate the crystals were unsuccessful.

In this case, as in the similar one studied by Beeson, the hydrogen reaction is the only one which takes place.

Decomposition of Paradiazotoluene Sulphate with Sodium Methylate.

52 grams of paradiazotoluene sulphate were decomposed with 200 cc. methyl alcohol in which 12 grams of sodium had been dissolved. The method of procedure was the same as in the case of the nitrate. The yield of oil was small—7.5

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[1] This JOURNAL, **16**, 244.

grams. On distilling, practically all of it came over at 109°–111°. The main product of the reaction was tar, from which nothing could be obtained. This was to be expected, for Beeson could get nothing but tar from the reaction between sodium methylate and diazobenzene sulphate.

The reaction in this case, as with the nitrate, is the hydrogen reaction exclusively.

Decomposition of Paradiazotoluene Nitrate with Methyl Alcohol and Caustic Potash.

45 grams of paradiazotoluene nitrate were decomposed with 200 cc. methyl alcohol, in which 20 grams of pure caustic potash had been dissolved. The diazo compound was added very slowly and in small portions, the flask being shaken after each addition. The decomposition took place immediately, but at first the action was very slow. Soon, however, enough heat was furnished by the reaction to make it necessary to moderate the action by cooling the flask. The whole was let stand over night, and the next day boiled for a short time on the water-bath, to insure complete decomposition. The alcohol was boiled off and the residue distilled with steam. By far the greater part of the oil came over with the alcohol. Yield of crude oil, 11 grams. Practically, the whole of this came over between 107° and 114°, and all but a few drops at 109°. A few drops of tarry oil remained in the bulb. The amount of tar left in the steam-flask was considerable.

The reaction is here, as was expected, entirely the hydrogen reaction.

Decomposition of Paradiazotoluene Sulphate with Methyl Alcohol and Caustic Potash.

In the same way 48 grams of paradiazotoluene sulphate were decomposed with 200 cc. methyl alcohol and 25 grams pure caustic potash. Yield of crude oil, 13 grams. This distilled over at 105°–115°. Nothing was done with the tar. Here, as before, the hydrogen reaction alone takes place.

Another experiment was performed, in which heat was applied. The decomposition took place very rapidly, and the products of the reaction were, besides tar, toluene and methoxytoluene in about equal quantities. This would tend to confirm the idea that heat is favorable to the alkoxy reaction.

Decomposition of Paradiazotoluene Nitrate with Methyl Alcohol and Potassium Carbonate.

In exactly the same way as above, 37 grams of paradiazotoluene nitrate were decomposed with 150 cc. methyl alcohol and 40 grams anhydrous potassium carbonate. The decomposition took place without the aid of heat. The alcohol was boiled off and steam passed through the residue. When the distillation with steam was nearly ended, a very little reddish oil containing crystals appeared in the condenser. The quantity was so small that nothing could be done with it. 11 grams of crude oil were obtained, which distilled over between 107° and 114°.

The effect of an alkaline carbonate upon the course of the reaction is, thus, the same as that of a caustic alkali.

Decomposition of Paradiazotoluene Sulphate with Methyl Alcohol and Potassium Carbonate.

40 grams of paradiazotoluene sulphate were decomposed with 300 cc. methyl alcohol and 40 grams anhydrous potassium carbonate. The method was the same as above given. Yield of crude oil, 10 grams. This proved to be toluene.

Decomposition of Paradiazotoluene Sulphate with Methyl Alcohol and Zinc Dust.

Beeson[1] obtained benzene and diphenyl as products of the decomposition of diazobenzene nitrate with methyl alcohol and zinc dust. The following experiments were made, to see whether the corresponding products would be formed in the case of diazotoluene sulphate and nitrate.

46 grams of paradiazotoluene sulphate were added gradually to 130 cc. methyl alcohol and an excess of zinc dust. Decomposition took place at once, and was moderated by putting the flask into ice-water. The products were treated with steam in the usual manner. Yield of crude oil, 9.5 grams. This proved to be toluene. No tar was observable in the steam-flask after the oil had all distilled over. The residue

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[1] This JOURNAL, **16**, 252.

was extracted with ether, in the hope that ditolyl might be obtained. On boiling off the ether about 5 grams of a clear, yellow, gummy substance were obtained, which was probably a complex mixture. All efforts to separate something which could be identified were unsuccessful.

Decomposition of Paradiazotoluene Nitrate with Methyl Alcohol and Zinc Dust.

Exactly as in the preceding experiment, 38 grams of paradiazotoluene nitrate were decomposed with 130 cc. methyl alcohol and an excess of zinc dust. The oily product proved to be toluene, and the yield was about the same as in the preceding experiment. The residue was extracted with ether, as before; nothing but tar was found.

During the course of this experiment it was noticed that when fresh zinc dust was added to the mixture of zinc dust, methyl alcohol and diazo compound, there was immediately a more rapid evolution of nitrogen, although an excess of zinc dust was already present. It was thought that perhaps this might be due to the more energetic action of the zinc oxide which is always present in small quantity in zinc dust. To test the influence of the oxide upon the course of the reaction, experiments were made with the diazo nitrate and sulphate with methyl alcohol in the presence of zinc oxide.

Decomposition of Paradiazotoluene Sulphate with Methyl Alcohol and Zinc Oxide.

44 grams of paradiazotoluene nitrate were added gradually to 200 cc. methyl alcohol and 20 grams powdered zinc oxide. No decomposition took place at the room temperature. The flask was placed in a water-bath, provided with a return-condenser, and heated slowly. Decomposition began at about 40°, and went on quietly and slowly, as when alcohol alone was used. After some time, however, the action had to be kept back by taking the flask out of the bath. The volatile products were separated in the usual way. The yield of crude oil was 10 grams. On fractionating, this was found to consist of about equal parts of toluene and methoxytoluene. The residue in the steam-flask was unpromising, and nothing was done with it.

Decomposition of Paradiazotoluene Sulphate with Methyl Alcohol and Zinc Oxide.

54 grams of paradiazotoluene sulphate were decomposed, as in the preceding experiment, with 250 cc. methyl alcohol and 20 grams powdered zinc oxide. The decomposition phenomena were similar to those in the case of the nitrate. After the decomposition had well begun, the mixture thickened and became quite pasty, and the bubbles of escaping nitrogen caused it to swell up so as nearly to fill the flask. After a time the mass became more liquid again. The products of decomposition were distilled with steam. Yield of crude oil, 17 grams. This consisted of about two parts of toluene and one of methoxytoluene.

Zinc oxide evidently does not influence the course of the reaction so strongly as does zinc dust. Just what is the full course of the reaction with zinc dust and with zinc oxide is not known. Want of time has prevented a more exhaustive study of these two reactions.

Comparison of Reactions.

The quantities obtained in the above described reactions are significant only in a general way, still it is of interest to compare them as far as the data will allow. The percentages of the theoretical yield are given.

	Paramethoxy-toluene.	Toluene.
Nitrate with alcohol, ord. pressure	29	trace
Sulphate " " "	66	trace
Nitrate " dim. "	22	10
Sulphate " " "	77	trace
Nitrate " incr. "	39	....
Sulphate " " "	61	trace
Nitrate with $NaOCH_3$	..	36
Sulphate "	..	32
Nitrate with alcohol and KOH	..	44
Sulphate " "	..	59
Nitrate " K_2CO_3	..	53
Sulphate " "	..	44
Nitrate " zinc dust	..	*
Sulphate " "	..	46
Nitrate " zinc oxide	17	22
Sulphate " "	20	48

* No record; about the same as the sulphate.

There may, of course, have been traces of methoxytoluene in those cases in which toluene was the only product found; but, as no method suggested itself for detecting traces of methoxytoluene in mixtures, no proof of its presence was found.

Summary of Results.

Several conclusions seem to be justified by the results of the experiments described in this paper.

1. The suggestion of Remsen and Dashiell,[1] that lowering of temperature and pressure tends to favor the hydrogen reaction, find support in the reaction of the diazo nitrate under diminished pressure. The sulphate, too, gives a better yield of methoxy product than the nitrate, and it decomposes at a higher temperature. But the sulphate gives a better yield of methoxy product as the pressure decreases. The largest percentage of methoxy product is given by the sulphate under reduced pressure.

2. The action of dilute nitric acid upon paramethoxytoluene, forming dinitrocresol, makes it probable that, in the cases in which nitrophenols are formed by the reaction of diazo nitrates with alcohol, these products are formed by saponification of the ethers first formed, the introduction of nitro groups taking place at the same time.

3. The fact that these diazo salts do not decompose rapidly at a low temperature in the presence of caustic potash was unexpected and surprising. It may find its explanation in the formation of isodiazo compounds similar to those first studied by Schraube and Schmidt.[2]

4. The results obtained by Beeson,[3] by the use of alkalies and of zinc dust, were found to hold good in all the cases studied, with the exception that no ditolyl was found. Any substance which will neutralize the acid liberated in the decomposition of the diazo compound will probably determine the hydrogen reaction, at least to some extent. This may be due to the fact that the reaction takes place at a lower temperature. When zinc oxide was used, the temperature at

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[1] This JOURNAL, **15**, 124.

[2] Ber. d. chem. Ges., **26**, 514.

[3] This JOURNAL, **16**, 252.

which decomposition took place was higher than in the other cases in which neutralizing agents were used, and the product was a mixed one, the reaction taking place in both ways. Why zinc should be more effective than zinc oxide, it is hard to say. Equations can be written which account for all the substances found, but they are of little value in the present state of knowledge.

XI.—THE REACTION OF SALTS OF THE NITRODIAZOBENZENES AND THE DIAZOBENZOIC ACIDS WITH METHYL ALCOHOL.[1]

BY GEORGE F. WEIDA.

The special object of this work was the study of the decomposition with methyl alcohol of the diazo compounds obtained from the three nitranilines and the three aminobenzoic acids, and the comparison of the results obtained with those obtained by Remsen and Graham[2] with the same diazo compounds and ordinary alcohol.

A. THE NITRODIAZOBENZENE SALTS.

1. *Orthonitrodiazobenzene Sulphate.*

Preparation of Orthonitraniline.—After trying various methods for the preparation of this substance, I should recommend the following as most advantageous :

The nitration is effected by the method of Körner—as described[3] by Remsen and Graham—except that a stronger nitric acid may be used. I found that by cooling properly, an acid of specific gravity 1.475–1.478 could be used without losing any considerable quantity of material by too rapid nitration. The contents of the beaker are now thrown into an evaporating-dish containing lumps of ice. The solid product is filtered from the ice-water as soon as practicable and treated as described by Remsen and Graham. But inasmuch as the filtrate contains the greater portion of the orthonitracetanilide,[4] it is very important to extract it and add it to the solid which has been filtered off from the ice-water. This is best effected by extraction of the filtrate with chloroform and subsequent evaporation of the chloroform extract. In the distillation with steam, utilize the saturated aqueous solution of orthonitraniline from the distillate to supply the boiler, according to the suggestion of Lellman. Avoid too great an excess of alkali to break off the acetyl group from the nitracetanilide, as prolonged boiling with excess of alkali is apt to yield nitrophenol.[3]

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[1] From the Author's Thesis, submitted to the Board of University Studies of the Johns Hopkins University for the Degree of Doctor of Philosophy, June, 1894.

[2] This JOURNAL, **11**, 319.

[3] *Loc. cit.*

[4] Grethen: Ber. d. chem. Ges., **9**, 775.

Preparation of Diazo Compouud from Orthonitraniline.—The nitraniline was suspended in dilute nitric or sulphuric acid, and, the vessel being placed in a freezing-mixture, a rapid current of nitrous fumes was passed through the mixture until it was saturated. I then added well cooled alcohol and ether to the solution, and after some time the diazo compound crystallized out. Inasmuch as sulphuric acid yielded the better results, I used the diazo compound obtained by mixing 45 cc. of the dilute and 5–8 cc. of strong sulphuric acid for every 10 gram portion af the orthonitraniline taken. 10 grams of nitraniline gave 14–15 grams of diazo compound.

Decomposition with Methyl Alcohol.—64 grams of the diazo compound, prepared as just described, were decomposed with 500 cc. methyl alcohol in three separate portions. The flask containing the alcohol and diazo compound was in each case connected with an inverted condenser, and then heated on the water-bath. Decomposition began as soon as the temperature of the water-bath reached 35°–40°—much lower than with the nitrates of the corresponding meta and para diazo compounds. At 60° the reaction went on very rapidly, and it was necessary to regulate the heat carefully. When the reaction became less vigorous the water in the bath was heated to 100°, and kept there for some time.

The products of decomposition from these flasks were united and the methyl alcohol distilled off on the water-bath. The liquid remaining in the flask was treated with an excess of an aqueous solution of caustic soda and subjected to distillation with steam. The distillate contained about 23 cc. of an oil, which (after drying with calcium chloride) had the boiling-point of nitrobenzene. 23 cc. of pure nitrobenzene (27.6

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[3] Ber. d. chem. Ges., 7, 76.

grams) corresponds to 87 per cent. of the theoretical yield from 64 grams of orthonitrodiazobenzene sulphate. No other definite chemical compounds were obtained either from the distillate or from the residue in the flask.

It is worthy of note that with this large yield of nitrobenzene the boiling-point of the product was much more constant than that of the oil obtained from the meta- and paranitrodiazobenzene nitrates.

2. *Metanitrodiazobenzene Nitrate.*

Decomposition with Methyl Alcohol.—After several preliminary tests with smaller quantities of diazo compounds, 120 grams of the substance were decomposed (in portions) by heating on the water-bath in a flask connected with an inverted condenser. The temperature was gradually raised to the boiling-point of water, and the heating was always continued for at least an hour—some considerable time after the evolution of gas had ceased. On cooling there was found in almost every case a beautiful yellowish-brown crystalline powder in a reddish liquid. The solid product was filtered off and its properties were studied. To my surprise it was found to be explosive and to behave in many respects as a diazo compound would do under similar conditions. Yet it seemed incredible that a portion of the diazo compound should remain unchanged after prolonged boiling with a large excess of methyl alcohol, and that it should crystallize out from the clear solution. When it was found, however, that it decomposed further with fresh portions of methyl alcohol (not only over the free flame, but even on the water-bath) it was concluded that such must be the case. The solid was accordingly decomposed with fresh portions of methyl alcohol, and the products of decomposition were added to the liquid before mentioned.

The united liquids representing the decomposition-products of 120 grams of metanitrodiazobenzene nitrate were treated as follows: The methyl alcohol was distilled off on the water-bath. 30 grams of caustic soda dissolved in 200 cc. of water were added to the residue to make it alkaline. On distillation with steam an abundance of an oily liquid passed over with the water, accompanied by a small quantity of a whitish powder. The latter portion of the distillate was caught separately, and from it after a time a few long needles crystallized out. These needles had the melting-point 37°, agreeing with that given for metanitranisol.[1] The other portions of light solid were recrystallized from alcohol and also had the melting-point 37°. This indicates the formation of small quantities of metanitroanisol.

The oil which came over with the first portions of the distillate was separated from water by means of a separating-funnel. It measured about 30 cc. After drying with calcium chloride, the greater portion distilled from 208°–210°, but some continued to come over at higher temperatures, almost up to 254°, the boiling-point of the nitranisol. If we assume that there were 36 grams of pure nitrobenzene, this would correspond to 51 per cent. of the theoretical yield if all the diazo compound could pass over into nitrobenzene.

After distillation with steam, the contents of the flask were acidified with dilute sulphuric acid, and were again subjected to distillation with steam. It was impossible, however, to isolate any further definite compounds either from this distillate or from the tarry residue remaining behind in the flask.

3. *Paranitrodiazobenzene Nitrate.*

First Decomposition with Methyl Alcohol.—Portions of about 20 grams of the diazo compound, prepared as just described, were decomposed with methyl alcohol, from 7–10 cc. of the alcohol being used for each gram of diazo compound. The flasks in which these portions were placed were connected with inverted condensers and heated on the water-bath. Decomposition began when the temperature of the water-bath reached about 60°. After the reaction became less marked, the temperature of the water-bath was gradually raised to 100°, and kept there for some time. The contents of each flask after the end of the decomposition consisted of a clear solution of the products of decomposition.

Three of these portions, corresponding to 57 grams of the diazo compound, were united and the methyl alcohol distilled off on the water-bath. The residue was made alkaline with about 13 grams of caustic soda dissolved in 300 cc. of water. This alkaline mixture was then subjected to distillation with steam. The receiver was well cooled with snow and ice, in order that any paranitranisol that came over might be obtained as a solid. The first portions of the distillate contained about 13 cc. of an oily liquid, which was shown by its boiling-point to be mostly nitrobenzene, but containing a small portion of a substance of high boiling-point, probably paranitranisol. Assuming a yield of 13 cc. (15.6 grams) of pure nitrobenzene, this would correspond to about 47 per cent. of the theoretical yield if all the diazo compound could pass over into nitrobenzene. The latter portions of the distillate contained a white solid in much greater quantity than was the case with the corresponding meta compound. It was collected and dried on filter-paper and found to weigh 3.2 grams. On purification it was found to correspond in melting-point,[1] etc., to the properties ascribed to paranitranisol. 3.2 grams of paranitranisol correspond to about 8 per cent. of the theoretical yield.

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[1] Bantlin: Ber. d. chem. Ges., 11, 2101.

Second Decomposition with Methyl Alcohol.—70 grams of the diazo compound were decomposed and the products of decomposition were treated as described above, except that more caustic soda was required to make the mixture alkaline. The products were the same as before, but in somewhat different proportions. About 13.5 cc. of the oil were obtained and 8.7 grams of the white solid product. As before, most of the oil boiled at the boiling-point of nitrobenzene, but the thermometer gradually rose, showing the presence of some small quantity of paranitranisol mixed with the nitrobenzene. In fact, I obtained some nitranisol from these portions of higher boiling-point and recrystallized it. This, as well as the main portion of the solid first obtained after recrystallization, was found to have the melting-point of paranitranisol[2] (53°). If the above named quantities are considered as representing pure nitrobenzene and nitranisol respectively, they correspond to about 40 per cent. of the theoretical yield for nitrobenzene, and 17 per cent. of the theoretical yield for the nitranisol.

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[1] J. prakt. Chem., **141**, 153.

[2] Willgerodt: J. prakt. Chem., **141**, 153.

B. THE SALTS OF THE DIAZOBENZOIC ACIDS.

1. *Orthodiazobenzoic-acid Nitrate.*

Preparation of the Diazo Compound from Anthranilic Acid.—The diazo compound was prepared according to the method of Griess[1] as follows: A pasty mixture of 10 grams of anthranilic acid (orthoaminobenzoic acid) with 50–60 cc. of nitric acid which had been previously diluted with an equal volume of water, was cooled in a freezing-mixture, and nitrous fumes were passed through it until everything had gone into solution, and there was an excess of nitrous acid present. About 150 cc. each of alcohol and ether were then added. The diazo compound separated out after stirring for some minutes. It was collected, washed with ether and dried in the usual manner. 10 grams of acid yielded from 10–11 grams of diazo compound. The product was yellowish, readily soluble in water, and when heated on platinum foil it exploded with a faint report.

Decomposition with Methyl Alcohol.—42 grams of diazo compound, prepared as just described, were placed in a flask and covered with about 200 cc. of methyl alcohol. The flask was connected with an inverted condenser, and heated on the water-bath. Decomposition began when the temperature of the bath reached 60° and went forward rapidly. After the methyl alcohol was distilled off, 100 cc. of water were added, and an oil sank beneath the water. Suspecting the formation of ethereal salts and wishing to separate them from any acid that might be volatile with steam, it was necessary to neutralize the free acid before distillation. In order to effect the neutralization without saponifying the ethereal salts, precipitated carbonate of calcium was used instead of the usual caustic alkali.

After carefully neutralizing all the free acid, the contents of the flask were subjected to distillation with steam. A yellow oil was separated from the aqueous portion of this distillate.

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[1] Ber. d. chem. Ges., 9, 1653.

and was found to measure about 10 cc. If this oil is an ethereal salt it is most probably either methyl benzoate, which boils at 199°, or the methyl ether of methylsalicylic acid (methyl orthomethoxybenzoate) which boils at 244°–246°. The oil was dried with calcium chloride and distilled. The thermometer rose gradually until it reached a maximum at 245°, and at this temperature the remainder of the oil distilled over. This shows that the oil is not a pure chemical individual, although it probably contains methyl orthomethoxybenzoate. The oil is not readily saponified by boiling with caustic alkali in a test-tube, but saponification is effected by boiling for some time in a flask connected with an inverted condenser. By diluting the strongly alkaline liquid thus obtained with water, and neutralizing with hydrochloric acid, a white acid was precipitated. Recrystallized from boiling water, it was obtained in beautiful crystals melting at about 88°. By repeated recrystallization the melting-point was raised to 99°. This therefore seems to be orthomethoxybenzoic acid, and confirms the probability that the oil from which it is obtained is mostly methyl orthomethoxybenzoate. The quantity of acid remaining after the repeated recrystallization was so small that it could not be investigated satisfactorily.

After the distillation with steam, the liquid remaining behind in the flask was also examined. Hydrochloric acid was added to it in order to set free any organic acid that might be present. An oily mass soon separated out. The supernatant liquid was poured off from the oil, and this liquid (after being allowed to stand for a number of hours) yielded yellowish crystals. The oil was an acid, as was shown by its behavior toward caustic alkalies; but it could not be purified sufficiently to determine its nature. The crystals from the liquid that had been poured off were repeatedly recrystallized from hot water, but on account of the small quantity they could not be purified sufficiently to establish their identity.

By decomposing a new portion (28 grams) of orthodiazobenzoic-acid nitrate with methyl alcohol, and neutralizing and distilling as before, the free acid was obtained in a much more satisfactory condition from the liquid remaining behind in the flask. It was found not to be volatile with water-vapor, and therefore it could not be benzoic acid. By boiling it with animal charcoal and repeatedly recrystallizing from hot water, it was obtained in large white needles, soon turning yellow. The melting-point 225°, and a blood-red coloration with ferric chloride made it seem probable that this substance is the unsymmetrical nitrosalicylic acid, the derivatives of which are described in detail by Hübner.[1] The same substance was probably obtained by Remsen and Graham[2] by the decomposition of orthodiazobenzoic acid nitrate in toluene. The small quantity of the product obtained prevented any further study of its properties than that above indicated.

2. *Orthodiazobenzoic-acid Sulphate.*

Preparation of the Diazo Compound from Anthranilic Acid.—On attempting to prepare this diazo compound as I did the salts of the other diazobenzoic acids—*viz.*, by diazotizing in dilute acid solution—I soon found that, although the amino compound dissolves readily when diazotizing, it is not an easy matter to precipitate out the diazo compound from this solution. I accordingly attempted to find a more satisfactory method. The method finally employed consisted in treating 10 grams of amino acid with about 15 cc. of concentrated sulphuric acid. After cooling in a freezing-mixture it was treated with about 100 cc. of alcohol, and then diazotized in the usual way. 10 grams of amido acid yielded in this way 17–18 grams of a beautiful white diazo compound.

Decomposition with Methyl Alcohol.—128 grams of diazo compound were decomposed with methyl alcohol, the alcohol distilled off, water added, the free acid neutralized, and the residue subjected to distillation with steam, as was described in detail in the case of the corresponding nitrate. About 35 cc. of an oil were obtained. When distilled, the thermometer passed from 200° to 246° during the process.

The acid obtained by the saponification of a portion of this oil did not have a sharp melting-point. The oil was then subjected to fractional distillation. The oil boiling from 200°–210° and that distilled from 240°–246° were saponified separately. The former yielded benzoic acid, melting at 120°; and the latter yielded methylsalicylic acid, melting at 99°.

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[1] Ber. d. chem. Ges., 8, 1217.

[2] This Journal, 11, 325.

3. *Metadiazobenzoic-acid Sulphate.*

Preparation of the Diazo Compound from Metaminobenzoic Acid.—The diazo compound was prepared according to the method of Griess,[1] except that I did not generally filter the mixture (after saturating with nitrous fumes) before precipitating out the diazo compound by means of alcohol and ether. The diazo compound was white at first, but it soon turned to a beautiful yellow. It seemed to be quite stable; a portion of it was kept over night without any apparent change. 10 grams of the metaminobenzoic acid yielded from 8-11 grams of the diazo compound, according to the conditions of the experiment.

Decomposition with Methyl Alcohol.—50 grams of the diazo compound, divided into several portions, were decomposed with methyl alcohol according to the method described in the case of the decomposition of the orthodiazobenzoic-acid nitrate. Decomposition began when the water-bath reached 60° and went forward quite rapidly. After the methyl alcohol was distilled off, water was added. The liquid in the flask arranged itself in two layers, an oil sinking below the water as in the case of the decomposition-products from the ortho compound. After distillation with steam, about 20 cc. of an oil were obtained from the distillate. Some trouble was experienced in drying this oil. On distillation, its boiling-point was found to be about 240°. The oil was saponified by boiling it with a concentrated aqueous solution of potassium hydroxide in a flask connected with an inverted condenser. The contents of the flask were diluted with water and the acid was set free by means of hydrochloric acid. The white solid was collected on a filter and freed from adhering liquid by means of a filter-pump. It was then recrystallized from boiling water. The product was an unusually beautiful one. The melting-point was found to be 106°, which agrees with that assigned to metamethoxybenzoic acid by Oppenheim and Pfaff.[2] The oil from which the acid is derived must therefore be regarded as an ethereal salt. No products other than methyl metamethoxybenzoate were obtained from the products of decomposition.

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[1] Ber. d. chem. Ges., **9**, 1655.

[2] *Ibid*, **8**, 887.

Decomposition with Ethyl Alcohol.—115 grams of diazo compound were decomposed with ethyl alcohol and the products of decomposition were treated in the same way as just outlined for the decomposition with methyl alcohol. About 30 cc. of a light-colored oil were obtained from the distillate. It boiled from 210°–211°, and, on saponification, yielded benzoic acid, which was recognized by its melting-point. This, together with the fact that aldehyde is given off during the decomposition, renders it evident that ethyl benzoate is the main product of the decomposition.

On distilling the oil carefully, however, the last few drops indicated a higher boiling-point. These were collected separately and saponified. By recrystallizing from a large excess of water (to separate from benzoic acid[1]) an acid having a melting-point of 136° was obtained, probably identical with the ethoxybenzoic acid described by Heintz.[2]

4. *Paradiazobenzoic-acid Nitrate.*

Preparation of the Diazo Compound from Paraminobenzoic Acid.—The diazo compound was prepared according to the method of Griess.[3] 10 grams of paraminobenzoic acid were treated with about 20 cc. of strong nitric acid. After cooling in ice-water, 20 cc. of dilute nitric acid were added, and the whole was shaken so as to form a pasty mixture. The flask was placed in a freezing-mixture of ice and hydrochloric acid and a rapid current of nitrous fumes was passed through the mixture until the contents of the flask went into solution. On adding to this 100 cc. of cold ether and about 75 cc. of cold alcohol, a precipitate of diazo compound was formed at once. The product was white, and in no case did I obtain it of the color of a light-brown sugar, as it is described by Remsen and Graham.[4] It was readily soluble in water and exploded when heated on platinum foil. 10 grams of aminobenzoic acid gave from 12 to 14 grams of diazo compound.

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[1] Griess: Ber. d. chem. Ges., **21**, 979.

[2] Ann. Chem. (Liebig), **153**, 334.

[3] *Ibid*, **120**, 126.

[4] This JOURNAL, **11**, 326.

Decomposition with Methyl Alcohol.—66 grams of the diazo compound, divided into several portions, were decomposed with methyl alcohol according to the method described in the case of the corresponding ortho compound. There was active decomposition when the temperature (60°) of the water-bath was reached. After the methyl alcohol was distilled off, and water added, the liquid in the flask arranged itself in two layers, an oil sinking below the water as in the case of the ortho compound. On distillation with steam for about two hours, the first product was a considerable quantity of an oil which soon turned solid. The later portions of the distillate were collected separately, and the product obtained was a white solid. Both products were found to be but sparingly soluble in water. On recrystallization, the two were found to be identical, each having the melting-point 48°—corresponding to the properties of the methyl paramethoxybenzoate described by Cahours.[1] The distillation with steam was not continued long enough to carry over all of this product.

The part remaining behind in the flask still consisted of an aqueous layer above a heavier oily liquid. The aqueous portion was separated while it was still warm, and set aside to crystallize. The crystals obtained from it were found to be impure anisic acid, but this portion was not purified, inasmuch as anisic acid was found elsewhere, as will be shown. The oily portion was poured into a distilling-bulb before it could solidify, and was subjected to distillation. A little water came over at first and then the thermometer rose rapidly to about 255°, the boiling-point of methyl paramethoxybenzoate. The portion boiling from 255°–260° was collected separately. A small portion of this distillate was saponified, and the anisic acid obtained from it was recrystallized from boiling water and its melting-point determined. The later portions of the distillate (boiling between 275° and 280°) were caught separately and a part was recrystallized from boiling water. The product was apparently not pure, so the free acid was dissolved by a solution of sodium carbonate, the solution filtered and the pure anisic acid precipitated by means of hydrochloric acid. The residue remaining behind on filtering the solution of the sodium salt was found to have the melting-point 47°, showing it to be the ethereal salt. The relative quantities of the products formed were not determined.

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[1] Ann. Chem. (Liebig), **56**, 311.

5. *Paradiazobenzoic-acid Sulphate.*

Preparation of the Diazo Compound from Paraminobenzoic Acid.—10 grams of the paraminobenzoic acid were treated with 30 cc. strong sulphuric acid, and after cooling, 60 cc. dilute sulphuric acid were added. This was cooled in a freezing-mixture, and a rapid current of nitrous fumes was passed through until the liquid became clear. The diazo compound was precipitated out promptly on the addition of ether and alcohol.

Decomposition with Methyl Alcohol.—77 grams of the diazo compound prepared as just described were decomposed with methyl alcohol in several portions as described under the orthodiazobenzoic acid. After distilling off the methyl alcohol a considerable quantity of crystals separated out from the liquid on cooling. This solid product was filtered off and was found to weigh 18 grams. Part of it was melted and distilled. Its boiling-point was determined to be about 250°. Another portion was saponified, yielding anisic acid. Still another portion was recrystallized and its melting-point was determined to be 48°. All these experiments indicate that the solid thus obtained is the methyl ether of anisic acid.

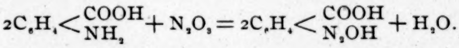
The filtrate from the crystals was subjected to distillation with steam, as the decomposition-products from the nitrate had been previously. Methyl paramethoxybenzoate (recognized by its pleasant anise-like odor and also by its melting-point) was found in the distillate. Methyl benzoate, if formed at all, is not formed in sufficient quantity to detect its presence with the quantities of material here employed. From the liquid remaining in the flask after distillation, a small quantity of an acid melting at about 177° was separated. This may have been impure anisic acid. But the free anisic acid, if formed at all in this reaction, is certainly much less in quantity than that formed with the corresponding nitrate.

Comparison of the Above Results with Those Obtained by Griess.—In an appendix to a paper on diazo compounds derived from the aromatic acids, Griess[1] says that these compounds are not formed at all when a large excess of nitrous acid is allowed to act on a hot alcoholic solution of the amido acid. Under these conditions a hydrogen atom is substituted for the amido group in the acid, nitrogen is liberated, and aldehyde and water are formed. He says: "In this way all the amido-acids that I have thus far had an opportunity to examine are converted into an acid which is identical or isomeric with that from which the amido acid is obtained by nitration and reduction of the nitro compound."

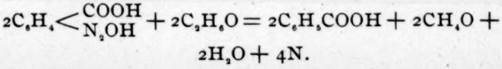
This was at a time when there was supposed to be more than one variety of benzoic acid; and Griess says that the "salylic acid" described by Kolbe and Lautemann[2] is the product obtained from amidobenzoic acid. He recommends the method above described as an admirable method for the preparation of salylic acid, the supposed isomer of benzoic acid. With the atomic weights at present used, the reactions he gives would become in the case of amidobenzoic acid:

$$2C_7H_7NO_2 + N_2O_3 + 2C_2H_6O = 2C_7H_6O_2 + 2C_2H_4O + 3H_2O + 4N.$$

If we wish to indicate the formation of the diazo compound we might represent the same facts by writing the two following reactions:



$$2C_6H_4<\begin{matrix}COOH\\NH_2\end{matrix} + N_2O_3 = 2C_6H_4<\begin{matrix}COOH\\N_2OH\end{matrix} + H_2O.$$



$$2C_6H_4<\begin{matrix}COOH\\N_2OH\end{matrix} + 2C_2H_6O = 2C_6H_5COOH + 2CH_4O + 2H_2O + 4N.$$

In a later paper[3] he describes more in detail his results in decomposing the sulphates of the three diazobenzoic acids with methyl alcohol as well as with ordinary alcohol. With methyl alcohol he obtained in the case of the ortho compound only benzoic acid, and in the case of both the meta and para compounds only methoxy acids. With ordinary alcohol he found that only the hydrogen reaction takes place in the case of the ortho compound, and both the hydrogen and ethoxy reaction, in the case of the meta and para compounds.

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[1] Ann. Chem. (Liebig), **117**, 63.

[2] *Ibid*, **115**, 187.

[3] Ber. d. chem. Ges., **21**, 979.

Fittica,[1] too, obtained the metethoxybenzoic acid from alcohol and metadiazobenzoic-acid sulphate.

With ordinary alcohol, Remsen and Graham[2] obtained ethyl benzoate as the principal product from the ortho and meta acids, and paraethoxybenzoic acid from the para acid. They also obtained the alkoxy reaction with methyl and propyl alcohols and paradiazobenzoic acids.

Excepting the formation of some methyl benzoate from orthodiazobenzoic acid sulphate, the tendency as shown by my experiments seems to be altogether toward the methoxy reaction, accompanied by a total or partial conversion of the methoxy acid into an ethereal salt. From methyl alcohol and the nitrate of orthodiazobenzoic acid under the conditions of the experiment described in this paper there is no free benzoic acid obtained. Further than this, it seems probable that the oil obtained is (as in the case of the sulphate), in part at least, an ethereal salt of the methoxy acid.

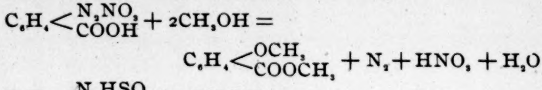
I am at a loss to explain the differences in the results obtained and shall make no attempts to reconcile them. From all the results it is however evident that methyl alcohol is more apt to give the alkoxy reaction than ordinary alcohol.

Summary.

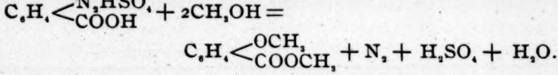
Orthonitrodiazobenzene sulphate yielded nitrobenzene as the only product of the reaction that can be isolated.

The para and metanitrodiazobenzene nitrates yielded mostly nitrobenzene, and some nitranisol.

The salts of the diazobenzoic acids all yielded as the principal product of the reaction with methyl alcohol the ethereal salts of the corresponding methoxy acids. Thus :



$$C_6H_4<\begin{matrix}N_2NO_3\\COOH\end{matrix}+2CH_3OH = C_6H_4<\begin{matrix}OCH_3\\COOCH_3\end{matrix}+N_2+HNO_3+H_2O;$$



$$C_6H_4<\begin{matrix}N_2HSO_4\\COOH\end{matrix}+2CH_3OH = C_6H_4<\begin{matrix}OCH_3\\COOCH_3\end{matrix}+N_2+H_2SO_4+H_2O.$$

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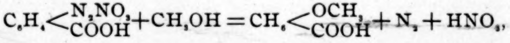
[1] Ber. d. chem. Ges., 11, 1209.

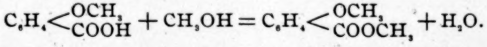
[2] This JOURNAL, 11, 325.

These processes probably take place in two steps: First, the decomposition of the diazo compound with the alcohol, yielding the corresponding methoxy acid, and then the formation of an ethereal salt by the action of the alcohol on the methoxy acid. In the case of the two nitrates the reactions would be



$$C_6H_4<\begin{array}{l}N_2NO_3\\COOH\end{array}+CH_3OH=CH_6<\begin{array}{l}OCH_3\\COOH\end{array}+N_2+HNO_3,$$

and

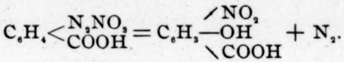


$$C_6H_4<\begin{array}{l}OCH_3\\COOH\end{array}+CH_3OH=C_6H_4<\begin{array}{l}OCH_3\\COOCH_3\end{array}+H_2O.$$

In the case of paradiazobenzoic acid nitrate, some of the free anisic acid was obtained.

With the *orthodiazobenzoic acid sulphate* some methyl benzoate is also formed together with the methyl methoxybenzoate, as was shown by fractional distillation of the oil and the fact that benzoic acid was obtained by saponification of the lower boiling portion.

With the *orthodiazobenzoic acid nitrate* some nitrosalicylic acid was obtained by loss of nitrogen and molecular rearrangement[1] thus:



$$C_6H_4<\begin{array}{l}N_2NO_3\\COOH\end{array}=C_6H_3\begin{array}{l}\diagup NO_2\\-OH\\\diagdown COOH\end{array}+N_2.$$

XII.—A STUDY OF THE ACTION OF METHYL ALCOHOL ON THE SULPHATE OF ORTHODIAZOTOLUENE.[2]

BY WILLIAM BROMWELL.

Preparation of Orthodiazotoluene Nitrate.

The method of Knoevenagel[3] for the preparation of dry diazo salts was tried as follows:

Fifteen grams of orthotoluidine nitrate were dissolved in about 350 cc. of alcohol and the solution acidified with a few drops of nitric acid and cooled to 0°. 12.5 grams of amyl nitrite were now added slowly while stirring. After standing about fifteen minutes, ether was added to aid the separation of the diazo compound. This experiment was repeated several times, but in no case could the diazo nitrate be obtained in this way, except in very small quantities. It was apparently decomposed as fast as formed, even though the temperature was kept at 0°. The solution became very dark and there was an evolution of nitrogen. The best yield was obtained by passing nitrous fumes, derived from the action of nitric acid upon arsenic, through the orthotoluidine nitrate mixed to a thin paste with alcohol, and kept cold by a freezing-mixture. After a time the salt went into solution, and finally a test with dilute caustic soda did not give the odor of toluidine. The action was then complete, and the solution was poured into strong alcohol (from lime), and ether slowly added with constant stirring till a permanent cloudiness resulted. As soon as the precipitation of the diazo compound commenced, more ether was added until no further precipitation was caused. The mixture was then allowed to stand for several hours, when the precipitate assumed a crystalline character, and was much more easily washed than when freshly precipitated, when it is usually somewhat gummy. It was then drained as completely as possible from the mother-liquor with the aid of the pump, and washed several times with cold absolute alcohol, and then with ether until the washings were colorless. The ether was then sucked off as completely as possible, and the crystals spread upon a porous plate to dry. When first washed with ether they were very light brown, but rapidly darkened upon exposure on a plate.

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[1] Remsen and Orndorff: This JOURNAL, **9**, 396.

[2] From the Author's Thesis, submitted to the Board of University Studies of the Johns Hopkins University for the Degree of Doctor of Philosophy, June, 1895.

[3] Ber. d. chem. Ges., **23**, 2994.

The first time the nitrate was prepared for this investigation, it remained on the plate for about twenty-four hours, when it became very dark and moist. On close examination it was found to be studded with minute fine yellow needles, and smelled strongly of cresol. While preparing to pick out some of these needles to determine their melting-point, the whole mass (about 38 grams) decomposed with violent explosion. The only apparent cause for the explosion was the heat from a Bunsen burner, which was burning at a distance of about twenty inches from the plate. The temperature could not have been raised more than a very few degrees.

A second lot of the nitrate (approximately 40 grams) was prepared in exactly the same way, and to avoid the possibility of an explosion care was taken to see that no flame was within ten feet of it. However, on taking it from the funnel and spreading it upon the porous plate to remove the last traces of ether, it immediately exploded with terrific violence, without any apparent cause. The force of the explosion was so great that the top of the table was badly shattered. All the gas burners in the room were extinguished, and the noise was so great that some of the men working in the room were temporarily deafened. The author's hand was injured to such an extent that it could not be used for about six weeks. As the nitrate was so unstable, upon resumption of work, the investigation was confined for the present to the sulphate.

Preparation of Orthodiazotoluene Sulphate.

The preparation of orthodiazotoluene sulphate is much more easily accomplished than that of the corresponding nitrate. The Knoevenagel method, that involving the use of amyl nitrite, was tried, and found to be very satisfactory, but the results were not materially better than those obtained by the use of the nitrous fumes from arsenic and nitric acid. The former is slightly quicker, but the presence of the amyl alcohol makes the recovery of the ordinary alcohol and ether more difficult. Therefore the following method, that used by Remsen and Orndorff[1] for this compound, and by Chamberlin[2] for the corresponding para compound, was adopted.

25 grams of pure orthotoluidine are dissolved in 250 cc. of ordinary alcohol in an Erlenmeyer flask, and a slight excess (25 grams) of sulphuric acid carefully added, drop by drop, with constant shaking until the orthotoluidine sulphate thus formed has dissolved. The flask is now placed in ice-water, and the fumes from nitric acid and arsenic, after passing through two wash-bottles immersed in ice-water, are conducted into the solution until the reaction is complete. This usually requires from one to two hours. The end of the reac-

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[1] This JOURNAL, 9, 394.

[2] See preceding article.

tion is best recognized by the appearance of the crystalline precipitate. The crystals of orthodiazotoluene sulphate are fine well-characterized needles, which are heavier than the irregular, flaky crystals of orthotoluidine sulphate. The action of the nitrous fumes is then stopped, the crystals filtered off, and to the filtrate ether is added when, after standing in an ice-bath for several hours, a second crop of crystals is obtained. The crystals are first washed with ordinary alcohol, and then with absolute alcohol till the washings are colorless. The alcohol is then washed out with anhydrous ether, which is sucked off as completely as possible with the pump. The salt is then spread out on a porous plate, and the last traces of ether rapidly disappear. Sometimes the salt has a bluish-green color; at others it is nearly white, turning pink on washing with alcohol. Exposed to the air on a porous plate at ordinary temperatures the salt is comparatively stable, no signs of explosion having been noticed, and only slight changes in color taking place in twenty-four hours.

The *methyl alcohol* used in these experiments was that sold as "Columbian Spirit," and obtained from H. C. Collier, Binghampton, N. Y. It was examined together with the best German methyl alcohol, and was found to compare very favorably with this, having slightly less of the empyreumatic odor. The German alcohol contained slightly less water than the "Columbian Spirit," but the following experiments show that there is little difference between them:

250 cc. each of the two kinds of methyl alcohol were treated with lime for eighteen hours and then distilled.

The German sample began to distil at 64°, and the temperature immediately rose to 65°.2, and remained at about 65° until all but the last few drops had come over. The "Columbian Spirit" started at 64° and rose steadily to 66°.

Now 50 cc. each of these distillates were redistilled. The German sample in this case distilled between 64°.5 and 65°, while the "Columbian Spirit" ranged from 64° to 66°, and just as the last few drops went off the temperature rose to 68°.

These experiments indicate that there was a little more water in the American specimen. Therefore the prolonged action of lime was tried, and it was found that, after standing for forty-eight hours, nearly all of a 750 cc. sample boiled exactly at 65° with a Hempel distilling-tube.

As this was perfectly satisfactory, the alcohol used in the following experiments was all prepared in this way from the "Columbian Spirit," the cost of which is just about one-fourth that of the imported article.

Action of Methyl Alcohol on Orthodiazotoluene Sulphate.

1. *At the Ordinary Room Temperature.*—About 30 grams of dry orthodiazotoluene sulphate were placed in a long-necked balloon-flask of about two liters' capacity, and treated with 100 cc. of methyl alcohol (from lime). The flask provided with a return-condenser was allowed to remain at the room temperature (about 20°). The action commenced at once, and there was quite a brisk evolution of nitrogen, but no perceptible odor of aldehyde. If the flask is left undisturbed the action is completed in about twenty hours, but it can be materially hastened by frequent shaking. It was then boiled on the water-bath for a short time to insure complete decomposition.

350 grams of orthodiazotoluene sulphate in portions of 30–40 grams were decomposed in this way with about 1400 cc. of methyl alcohol. The various portions were united and the alcohol distilled off on the water-bath. This distillate was added to about five times its volume of a saturated solution of common salt, when an oil of a pale yellow color slowly separated and rose to the surface. Water was then added to the residue remaining in the flask, and the distillation continued with steam. A yellow oil distilled over with the water. Its specific gravity is very nearly that of water. The residue in the flask consisted of a clear liquid and a black tarry substance, which later became quite hard and brittle upon cooling. The temperature was reduced to 0°, and the liquid filtered off and evaporated. Nothing except sulphuric acid was found in the residue. The tar, a black, solid mass, was extracted with alcohol, and most of it went into solution, but nothing was obtained from it.

The oils were then washed and dried over calcium chloride. They both have the same pleasant, aromatic odor, suggesting that of the oil of wintergreen, but still quite different from it.

35 grams of the oil were obtained in this way from the alcoholic distillate. On distilling this, only a few drops came over as the thermometer went steadily up to 160°, nearly all coming over between 164° and 174°, only about 1 gram being left in the flask at 174°.

97 grams of the oil were obtained from the steam distillate; 73 grams came over between 164° and 170°; and most of the rest between 170° and 174°, leaving as above, only about 1 gram in the flask. These two portions of oil, boiling between 164° and 174°, being apparently identical, were united and set aside.

2. *At a Temperature near that of the Boiling-Point of the Alcohol.*—400 grams of the orthodiazotoluene sulphate were decomposed by heating the flask, provided with a return-condenser and containing about 30 grams of the salt and about 100 cc. of absolute methyl alcohol, on the water-bath at about 50°–60° for about half an hour, when the action was apparently complete. The contents of the flask were then boiled for a few minutes to insure complete decomposition. The various portions decomposed in this way were united, and were treated exactly as in the preceding experiment. The alcohol was distilled off, and 46 grams of oil were obtained from the alcoholic distillate on treatment with a strong solution of common salt.

The distillation was then continued with steam, and 115 grams of the oil were thus obtained.

The oil obtained from the alcoholic distillate was washed, dried, and distilled, nearly all of it coming over between 164° and 174°.

The oil from the steam distillate was then treated in the same way, and nearly all of it came over between the same points, only about 5 grams coming over below 160° and about 12 grams above 174°, from both the portions.

The oil from all the various portions was then brought together and fractionated, and it was found that of the 293 grams of oil obtained altogether, 247 grams (over 84 per cent.) distilled between 167° and 170°. The average boiling-point of this portion, (168°.5) corrected for the column of mercury outside of the vapor of the oil, is 171°.35.

The boiling-point of the methyl ether of orthocresol, $C_6H_4 < \begin{matrix} CH_3 \\ OCH_3 \end{matrix}$, as given by Pinnette[1] is 171°.3. Thus it will be seen that the principal action of methyl alcohol on orthodiazotoluene sulphate is expressed by the following equation:

$$C_6H_4 < \begin{matrix} CH_3 \\ N_2.HSO_4 \end{matrix} + CH_3OH = C_6H_4 < \begin{matrix} CH_3 \\ OCH_3 \end{matrix} + H_2SO_4 + N_2.$$

This corresponds to the decomposition of the same diazo salt with ordinary alcohol, as observed by Remsen and Orndorff,[2] who obtained as the chief product the ethyl ether of orthocresol. If toluene was formed, it was in such small quantities as to escape their notice. In these experiments, however, in which larger quantities were used, there was enough of the oil boiling below 130° to enable us to prove the presence of toluene. This was done by adding a few drops of the oil to hot fuming nitric acid and pouring the mixture into water. On standing, crystals separated out which melt at 55°, and are, therefore, paranitrotoluene. No odor of formic aldehyde was observed during any of the decompositions. Apparently there was slightly more of the low-boiling oil formed in the second experiment where the decomposition was effected at the higher temperature, though the difference was so slight, and the quantities of toluene so small in both cases that no conclusion of value could be drawn.

Orthomethoxytoluene, or the Methyl Ether of Orthocresol.

The methyl ether of orthocresol was made by Pinnette[3] from phenol, potassium hydroxide, and methyl iodide, according to the Williamson reaction, and is described by him only as boiling at 171°.3, and as having the specific gravity 0.9957 at 0°. In consideration of the fact that this is the only knowledge we have of the substance, it was thought well to study it a little further. It is a colorless, very highly refracting, mobile oil, with a rather pleasant, aromatic odor, as above described, suggesting the oil of wintergreen, though differing markedly from it. It is almost insoluble in water, but easily soluble in alcohol and ether.

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[1] Ann. Chem. (Liebig), **243**, 37.

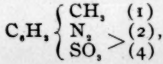
[2] Am. Chem. J., **9**, 387.

[3] Ann. Chem. (Liebig), **243**, 37.

Action of Sulphuric Acid on Orthomethoxytoluene.

Forty grams of orthomethoxytoluene were poured slowly into 120 grams of concentrated sulphuric acid. Action took place at once, the oil going into solution with the formation of a decided rose color. The mixture was shaken for a few minutes to insure complete reaction, and it was then poured into about a liter and a half of water, and neutralized with barium carbonate. The salt thus obtained was recrystallized, and the appearance of the crystals, which were small, transparent, glistening plates, and also still smaller white granules, suggested the possibility of two sulphonic acids.

Therefore, the salt was subjected to careful and prolonged fractional crystallization. Specimens of the salts from the extremes and from the middle of the series of fractions were taken, and from these were made first the sodium salts. These were treated with phosphorus pentachloride, and the sulphone chlorides obtained. These were solid and were apparently all the same. They were now treated with ammonia, and the amides were thus made and recrystallized. All three amides melt sharply at 137°, and are therefore derived from the same sulphonic acid. This in turn shows that the result of treating the methyl ether of orthocresol is beyond doubt only one sulphonic acid. As this acid has not been described in the literature, it was decided to make and study some of its salts and derivatives.

Hayduck[1] decomposed the diazo compound of the formula,  $C_6H_3\begin{cases}CH_3 & (1)\\ N_2 & >(2)\\ SO_3 & >(4)\end{cases}$, with methyl alcohol, and obtained orthomethoxyparatoluenesulphonic acid, the barium salt of which he describes as crystallizing in small shining plates with two molecules of water of crystallization, which it does not lose over sulphuric acid.

The barium salt to be presently described as made from orthomethoxytoluene by treatment with sulphuric acid and neutralizing with barium carbonate, agrees closely with that made by Hayduck. The latter, as above mentioned, crystallized in whitish, irregular crystals mixed with shining transparent plates. In the course of fractional crystallization it is observed that it depends largely on the concentration of the solution which kind of crystals predominates. If the solution is comparatively weak, the crystals are nearly all shining plates; but if the solution is quite concentrated the white opaque crystals are the rule. In a sample of the shining plates the water of crystallization was determined and found to correspond closely to the formula

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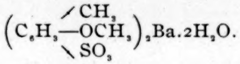
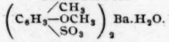
[1] Ann. Chem. (Liebig), 172, 217.



$$\left(C_6H_3\begin{array}{l}\diagup CH_3\\ —OCH_3\\ \diagdown SO_3\end{array}\right)_2Ba.2H_2O.$$

Calculated 6.26 Found 6.18

In another sample of the opaque variety the water and barium were estimated with the following results:

	Calculated for  $\left(C_6H_3\begin{array}{l}\diagup CH_3\\ —OCH_3\\ \diagdown SO_3\end{array}\right)_2Ba.H_2O.$	Found.
H_2O	3.23	3.83
Ba	24.43	24.37

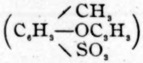
It will thus be seen that the salt crystallizes sometimes with one and sometimes with two molecules of water of crystallization. It is also almost impossible to obtain a crop of crystals entirely of either form. For this reason the analyses do not give especially good results.

Remsen and Parks[1] noted a similar influence of the concentration of the solution on the crystallization of the barium salt of paramethoxyorthotoluenesulphonic acid.

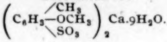
Orthomethoxytoluenesulphonic Acid.—As it seemed desirable to make a further study of this acid and its salts, some of the free acid was prepared by exactly neutralizing a solution of the barium salt with dilute sulphuric acid. The barium sulphate was filtered off, and the filtrate evaporated to a small bulk. The acid is very soluble in water, and in order to make it crystallize a few drops of a saturated solution of com-

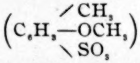
[1] This JOURNAL, **15**, 320.

mon salt were added as recommended by Gattermann,[1] whereupon crystallization immediately commenced with the formation of beautiful, stellate clusters of short needles throughout the whole solution. The acid is filtered off, and, when dried, found to melt at 212°.

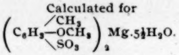


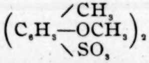
Calcium Salt, $\left(C_6H_3\begin{array}{l}\diagup CH_3\\ -OC_3H_3\\ \diagdown SO_3\end{array}\right)_2Ca.9H_2O$. — This salt is very soluble in water and slightly less so in alcohol. From water it crystallizes in large, colorless, transparent plates, which are very efflorescent. Analyses for water and calcium gave the following results :

	Calculated for  $\left(C_6H_3\begin{array}{l}\diagup CH_3\\ -OCH_3\\ \diagdown SO_3\end{array}\right)_2Ca.9H_2O$.	Found. I.	Found. II.
H_2O	26.82	26.82	26.51
Ca	6.62	6.60	6.68

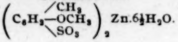


Magnesium Salt, $\left(C_6H_3\begin{array}{l}\diagup CH_3\\ -OCH_3\\ \diagdown SO_3\end{array}\right)_2Mg.5\frac{1}{2}H_2O$.—This salt is easily soluble in water, but crystallizes well from it in large, well-developed, colorless, transparent prisms, which are not changed by exposure to the air. Analyses for water and magnesium gave the following results :

	Calculated for  $\left(C_6H_3\begin{array}{l}\diagup CH_3\\ -OCH_3\\ \diagdown SO_3\end{array}\right)_2Mg.5\frac{1}{2}H_2O$.	Found. I.	Found. II.
H_2O	18.85	19.11	19.03
Mg	4.57	4.56	4.42



Zinc Salt, $\left(C_6H_3\begin{array}{l}\diagup CH_3\\ -OCH_3\\ \diagdown SO_3\end{array}\right)_2Zn.6\frac{1}{2}H_2O$.—This salt crystallizes from water, in which it is easily soluble, in large, colorless, transparent rectangular plates, which lose part of their water on exposure to the air. Analyses for water and zinc gave the following results :

	Calculated for  $\left(C_6H_3\begin{array}{l}\diagup CH_3\\ -OCH_3\\ \diagdown SO_3\end{array}\right)_2Zn.6\frac{1}{2}H_2O$.	Found. I.	Found. II.
H_2O	20.03	19.42	19.84
Zn	11.13	10.70	10.98

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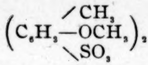
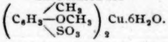
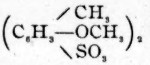
[1] Ber. d. chem. Ges., **24**, 2121.



Copper Salt, $\left(C_6H_3\begin{array}{l}\diagup CH_3\\ -OCH_3\\ \diagdown SO_3\end{array}\right)_2Cu.6H_2O$.—The crystals are small, transparent, apple-green prisms, many of which have an apparently hexagonal section. They are easily soluble in water and are quite stable in the air. Analyses for water and copper gave the following results :

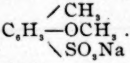
	Calculated for  $\left(C_6H_3\begin{array}{l}\diagup CH_3\\ -OCH_3\\ \diagdown SO_3\end{array}\right)_2Cu.6H_2O$.	Found. I.	Found. II.
H_2O	18.85	18.62	18.52
Cu	10.99	10.74	10.64



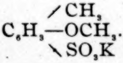
Lead Salt, $\left(C_6H_3\begin{array}{l}\diagup CH_3\\ -OCH_3\\ \diagdown SO_3\end{array}\right)_2Pb.6H_2O$. — This salt crystallizes from its water solution in thin leaflets with a pearly luster. These lose water, and with it their luster, on exposure to the air. This salt is quite unstable, decomposing within a few degrees of the point at which it ceases to give off water of crystallization, *i. e.*, approximately at 115°.

Much difficulty was experienced in the analysis of this salt both for the water, on account of the above-mentioned fact, and also for the lead, because of the ease with which lead sulphate is reduced. The analysis was most satisfactorily made in the following manner: The salt is weighed into a porcelain crucible and heated in the air-bath to about 110° to constant weight. It is now treated with a drop of sulphuric acid and one or two drops of nitric acid and heated carefully. When dry, more nitric acid is added as needed to oxidize the carbon. When this is accomplished a few drops of aqua regia are added and the crucible *very* gently heated for some time. Then sulphuric acid is added and evaporated repeatedly at as low a temperature as possible. It is finally brought to a dull red heat, until the free sulphuric acid has all been driven off. It is then cooled and weighed. The results were low in every case, and only by working with the utmost care, as above described, could approximate results be obtained.

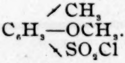
	Calculated for $\left(C_6H_3\begin{array}{l}\diagup CH_3\\ -OCH_3\\ \diagdown SO_3\end{array}\right)_2 Pb.6H_2O.$	Found.
H_2O	15.06	15.50
Pb	28.77	28.54

Sodium Salt,  $C_6H_3\begin{array}{l}\diagup CH_3\\ -OCH_3\\ \diagdown SO_3Na\end{array}.\ 5\frac{1}{2}H_2O.$ — This salt crystallizes in large colorless, transparent needles, which rapidly lose water on exposure to the air. Analyses for water and sodium gave the following results:

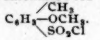
	Calculated for $C_6H_3\begin{array}{l}\diagup CH_3\\ -OCH_3\\ \diagdown SO_3Na\end{array}.\ 5\frac{1}{2}H_2O.$	Found. I.	Found. II.
H_2O	30.65	29.53	29.22
Na	10.27	10.21	10.89

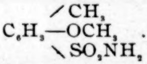
Potassium Salt,  $C_6H_3\begin{array}{l}\diagup CH_3\\ -OCH_3\\ \diagdown SO_3K\end{array}.\ \frac{1}{2}H_2O.$—This is so very easily soluble in water that it was found to be impossible to obtain it well crystallized from that solvent. It is much less easily soluble in alcohol, and from this it is obtained under certain conditions, in small, transparent, rhombic plates. Analyses for water and potassium gave the following results:

	Calculated for $C_6H_3\begin{array}{l}\diagup CH_3\\ -OCH_3\\ \diagdown SO_3K\end{array}.\frac{1}{2}H_2O.$	Found.
H_2O	3.61	3.91
K	16.25	16.31

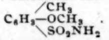
Orthomethoxytoluenesulphone Chloride,  $C_6H_3\begin{array}{l}\diagup CH_3\\ -OCH_3\\ \diagdown SO_2Cl\end{array}.$ — The sodium salt was thoroughly dried in the air-bath at 120° and powdered. After cooling it was treated with a slight excess of phosphorus pentachloride. Action was brought about by rubbing the two together in a dry evaporating-dish with a dry pestle. Action took place quite readily, and after it was over and the mixture had cooled, cold water was added, when the chloride, which was at first soft, became quite hard and brittle, so that it was easily powdered and washed. A part of this was now dissolved in ether, from which it solidified in a compact, white, crystalline mass.

An estimation of chlorine gave the following result:

	Calculated for  $C_6H_3\left\langle\begin{matrix}CH_3\\OCH_3\\SO_2Cl\end{matrix}\right.$.	Found.
Cl	16.78	16.34

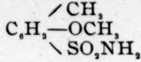
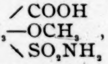
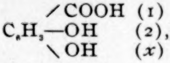
Orthomethoxytoluenesulphonamide,  $C_6H_3\left\langle\begin{matrix}CH_3\\OCH_3\\SO_2NH_2\end{matrix}\right.$. — This was made by treating the sulphone chloride, which has just been described, with ammonia, and allowing the mixture to stand for several hours. Most of the ammonia was now evaporated off, as the sulphonamide was found to be somewhat soluble in it. On cooling, the crystals were separated from the mother-liquor, and recrystallized from hot water.

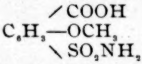
As thus obtained, they are beautiful, fine, white needles, which melt at 137°. Analyses gave the following results:

	Calculated for  $C_6H_3\left\langle\begin{matrix}CH_3\\OCH_3\\SO_2NH_2\end{matrix}\right.$.		Found.	
		I.	II.	III.
N	6.98	7.13	7.18	7.04
C	47.73	47.69	...	...
H	5.64	5.43	...	...

The figures under I. for nitrogen, carbon, and hydrogen, were kindly furnished by Mr. C. D. Ragland. The nitrogen in this, as in the second case by Messrs. J. W. Lawson and E. S. Smith, was estimated by the Dumas method. The third estimation of nitrogen, furnished by Mr. Lawson, was made by the Kjeldahl method.

Constitution of Orthomethoxytoluenesulphonic Acid. — From a study of the compound, it was seen that when orthomethoxytoluene is treated with sulphuric acid only one acid residue enters into the compound.

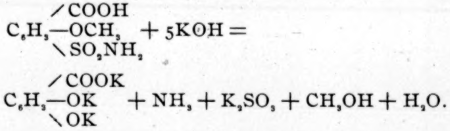
In order to determine the position of the sulphonic acid residue, it was thought that it would be easy to pass from the sulphonamide,  $C_6H_3\left\langle\begin{matrix}CH_3\\OCH_3\\SO_2NH_2\end{matrix}\right.$, to orthomethoxysulphaminebenzoic acid,  $C_6H_3\left\langle\begin{matrix}COOH\\OCH_3\\SO_2NH_2\end{matrix}\right.$, by oxidation with potassium permanganate; and from this, by fusion with potassium hydroxide, to one of the four possible dihydroxybenzoic acids,  $C_6H_3\begin{array}{l} \diagup COOH \ (1) \\ —OH \quad (2) \\ \diagdown OH \quad (x) \end{array}$, which are known. To accomplish this the following experiments were performed:

Formation of Orthomethoxysulphaminebenzoic Acid.—Ten grams of the sulphonamide, as formed above, were treated with 34 grams of potassium permanganate in about a liter of water. These were heated in a balloon-flask with a return-condenser from eight to ten hours, when the permanganate was completely reduced. In case this should not be so, a few drops of alcohol may be added to complete the reduction. The oxides of manganese were now filtered off, and the solution containing the potassium salt of the acid was evaporated to a small volume. It was then acidified with hydrochloric acid, when the free acid,  $C_6H_3\begin{array}{l} \diagup COOH \\ —OCH_3 \\ \diagdown SO_2NH_2 \end{array}$, crystallized out. This was filtered off and dissolved in a dilute solution of sodium carbonate to separate it from any amide which remained unoxidized. It was filtered, reprecipitated with hydrochloric acid, again filtered, recrystallized, and analyzed for sulphur and nitrogen with the following results:

	Calculated.	Found.
S	13.81	13.85
N	6.06	6.67

The melting-point is 211°.

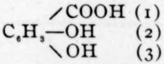
Formation of Dihydroxybenzoic Acid.—To about 10–12 grams of potassium hydroxide, in a silver crucible, a few drops of water were added. Heat was then gently applied, and the sulphaminebenzoic acid was added gradually. Care was taken to keep the temperature as little above the melting-point of the mixture as possible during the reaction, in order to avoid breaking up the carboxyl group with the elimination of carbon dioxide. The mixture was heated until a few drops of it, dissolved in a little water, gave off sulphur dioxide when treated with hydrochloric acid. The mass was then allowed to cool, dissolved in water and acidified. It was then evaporated to crystallization, cooled, filtered. When recrystallized the product appeared either as moderately large needles or as very small, short prisms. The changes which were expected here arerepresented by the equation:



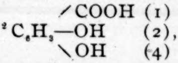
$$C_6H_3\begin{array}{l}\diagup COOH\\ —OCH_3\\ \diagdown SO_2NH_2\end{array} + 5KOH = C_6H_3\begin{array}{l}\diagup COOK\\ —OK\\ \diagdown OK\end{array} + NH_3 + K_2SO_3 + CH_3OH + H_2O.$$

The substance thus obtained was well crystallized and melted fairly well at about 230° with evolution of gas. A drop of a solution of ferric chloride added to a very dilute aqueous solution of the compound gave a deep red color. It did not reduce Fehling's solution.

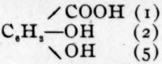
Now upon studying the four known dihydroxybenzoic acids, with one of which it might be possible for this to be identical, we find that their characteristic properties are as here given:



The 1, 2, 3 acid,[1] $C_6H_3\begin{array}{ll}\diagup COOH & (1)\\ —OH & (2)\\ \diagdown OH & (3)\end{array}$, melts at 204° and is colored dark blue by a solution of ferric chloride. It crystallizes in "water-free warts" or in needles with two molecules of water.



β-Resorcylic acid, the unsymmetrical metadihydroxybenzoic acid,[2] $C_6H_3\begin{array}{ll}\diagup COOH & (1)\\ —OH & (2)\\ \diagdown OH & (4)\end{array}$, when free from water, melts according to different observers, at 194°, 197°, 194°–200°, 204°–206°, and 213°. It is described as crystallizing with $\frac{1}{2}$, $1\frac{1}{2}$, $2\frac{1}{2}$, and 3 molecules of water according to circumstances. It does not reduce Fehling's solution. When heated above its melting-point it loses carbon dioxide and is converted into resorcin.



Oxysalicylic acid, $C_6H_3\begin{array}{ll}\diagup COOH & (1)\\ —OH & (2)\\ \diagdown OH & (5)\end{array}$, melts according to various authorities, at 196°–197°, or 199°–200°. Ferric chloride colors its solution deep blue. It reduces Fehling's solution.

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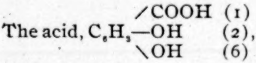
[1] Ann. Chem. (Liebig), **220**, 116.

[2] Ann. Chem. (Liebig), **161**, 11; This JOURNAL, **2**, 169; Ber. d. chem. Ges., **18**, 1985.



The acid, $C_6H_3\begin{array}{ll}\diagup COOH & (1)\\ -OH & (2)\\ \diagdown OH & (6)\end{array}$, is described by Senhofer and Brunner.[1] It melts from 148°–167°. Its solution is colored violet by ferric chloride, and it reduces Fehling's solution.

All of these acids give off carbon dioxide, forming the corresponding dihydroxy derivative of benzene.

It will be observed that the compound obtained by fusing orthomethoxysulphaminebenzoic acid with potassium hydroxide does not correspond to any of these acids. It agrees with β-resorcylic acid (1, 2, 4) in being colored red by ferric chloride, and in not reducing Fehling's solution. But its melting-point is too high, and it does not form fluoresceïn when heated with phthalic anhydride. It is suspected that the substance is not pure, and qualitative tests for sulphur and nitrogen show the presence of both. This indicates that the fusion with potassium hydroxide was not complete. Therefore, what remained of the substance was again fused with potassium hydroxide. This time the temperature was raised somewhat higher than before, and the fusion continued for about ten minutes. The mass, on cooling, became yellowish-brown. This was dissolved in water, evaporated and extracted with ether. The residue consisted of a crystalline crust on the beaker, which was studded with fine, white needles. The former melted at about 130° and the latter at 155°. Both portions were carefully tested with phthalic anhydride for resorcin, but no trace of fluoresceïn was formed. With ferric chloride the color was exactly that given by salicylic acid, and not that given by resorcin. In order to separate the acid from the dihydroxybenzene, in case they should both be present, the substance was treated with a solution of sodium carbonate, and then extracted with ether, which would take the dihydroxy derivative and leave the sodium salt of the acid in the water. The ether extract was evaporated, leaving a small impure residue which melts through a range of 15°, from 120°–135°.

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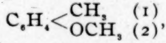
[1] Wiener Akademieber., (1879), 80.

The ferric chloride color reaction was exactly that of salicylic acid. It is difficult to account for any salicylic acid here.

The small amount of material and the lack of time makes a further study of this question impossible at this time.[1]

Oxidation of Orthomethoxytoluene.—In order to furnish additional evidence that the formula of the oil obtained by the decomposition of orthodiazotoluene sulphate by methyl alcohol is  $C_6H_4\begin{matrix} < CH_3 & (1) \\ < OCH_3 & (2) \end{matrix}$, some of the oil was oxidized as follows:

Thirteen grams of potassium permanganate were dissolved in about 700 cc. of water in a flask fitted with a return-condenser, and 5 grams of the oil were added. The mixture was heated on the water-bath, with frequent shaking, for about three hours, when the reduction of the permanganate was complete. The oxides of manganese were filtered off and the clear solution evaporated to about 100 cc. This was then acidified with hydrochloric acid. On cooling, beautiful, fern-like crystals separate. After recrystallization these melt at 98°.5–99°, thus agreeing closely with orthomethoxybenzoic acid, which is described by Cahours[2] as melting at 98°.

Conclusions.

This investigation shows:

1. That orthodiazotoluene sulphate is decomposed by methyl alcohol at a lower temperature than the corresponding para compound.
2. That orthodiazotoluene sulphate, when decomposed by methyl alcohol under atmospheric pressure, gives almost exclusively the alkoxy reaction.
3. That, whether the decomposition takes place slowly at the temperature of the room, or rapidly at a temperature near the boiling-point of the alcohol, the yield of the methoxy product is practically the same.
4. That when orthomethoxytoluene is treated with cold concentrated sulphuric acid only one sulphonic acid is formed.
5. That the sulphonic acid so formed is a monobasic acid containing only one sulphuric acid residue.
6. That by oxidation, orthomethoxytoluene yields orthomethoxybenzoic acid.

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[1] See the following article.—I. R.

[2] Ann. Chem. (Liebig), **42**, 60; *Ibid*, **92**, 315.

ON THE ACTION OF POTASSIUM HYDROXIDE ON ORTHOMETHOXYSULPHAMINEBENZOIC ACID.

BY CHARLES WALKER.

In the preceding article, by Mr. Bromwell, an experiment is described, the results of which are not clear. In order to determine the constitution of the sulphonic acid formed by the action of sulphuric acid on orthomethoxytoluene the acid was converted into the corresponding amide, and this oxidized. The sulphaminebenzoic acid thus obtained,

$$C_6H_3\left\{\begin{array}{l}COOH\\OCH_3\\SO_2NH_2\end{array}\right.,$$

was then fused with potassium hydroxide in the expectation that it would be converted into the corresponding dihydroxybenzoic acid. The product was, however, shown not to be a dihydroxybenzoic acid, and the investigation was not carried any farther. At this point I took it up at the suggestion of Professor Remsen, and the results are here communicated.

From 10 to 13 grams of caustic potash were placed in a silver crucible with a little water, and, after heating gently, 3 grams of the acid were added. The fusion was continued at low redness for from five to eight minutes, the mass cooled and dissolved in water. On acidifying, a white crystalline precipitate was obtained. After crystallizing from water a number of times it was analyzed.

I. 0.2145 gram substance gave 0.3021 gram CO_2 and 0.0694 gram water.

II. 0.2522 gram substance gave 0.3569 gram CO_2 and 0.0772 gram water.

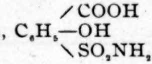
III. 0.2066 gram substance gave 12.3 cc. nitrogen at 758 mm. and 25°.

IV. 0.2452 gram substance gave 16.6 cc. nitrogen at 759 mm. and 30°.

V. 0.1740 gram substance gave 0.1901 gram $BaSO_4$.

	Calculated for $C_7H_7NSO_5$.	Found.				
		I.	II.	III.	IV.	V.
C	38.71	38.41	38.59	....	....	....
H	3.22	3.59	3.40	....	....	....
N	6.45	....	....	6.79	6.66	....
S	14.75	....	....	....	....	15.00

The combustions were made with a mixture of potassium dichromate and lead chromate.

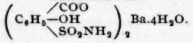
The substance, therefore, is orthoxysulphaminebenzoic acid,  $C_6H_3\begin{cases}\diagup COOH\\ -OH\\ \diagdown SO_2NH_2\end{cases}$. It crystallizes from water in white needles, which melt at 231° with decomposition. In aqueous solution with ferric chloride it gives a red coloration.

The great stability of the sulphamide group in this compound is worthy of special note. Another case of the same kind has since been brought to light in this laboratory.

Barium Salt.—The barium salt was prepared by treating the acid suspended in water with pure and finely divided barium carbonate. It crystallizes from water in aggregates of crystals of fine, white needles. After drying in the air it was analyzed.

0.9031 gram of the salt heated 15 hours at 150°–160° lost 0.1040 gram.

0.2620 gram of the anhydrous salt gave 0.1070 gram $BaSO_4$.

Calculated for  $\left(C_6H_3\begin{cases}\diagup COO\\ -OH\\ \diagdown SO_2NH_2\end{cases}\right)_2 Ba.4H_2O.$	Found.
11.23	11.51
25.08	24.01

Calcium Salt.—This was prepared from Iceland spar in the same way as the barium salt. It crystallizes from aqueous solution in long fibrous needles. The water of crystallization and calcium were determined with the following results:

1.3090 grams heated fourteen hours, at 120°–125°, lost 0.2487 gram.

0.5435 gram anhydrous salt gave 0.1515 gram $CuSO_4$.

	Calculated for $(C_7H_6NSO_5)_2Ca + 6H_2O$.	Found.
H_2O	18.62	18.99
Ca	8.48	8.20

Sodium Salt.—The sodium salt was made from the barium salt by adding the calculated amount of sodium carbonate to the aqueous solution of the barium salt. It separates from aqueous solution in short, white needles. Determinations of water of crystallization and sodium were made with the following results:

1.5088 grams heated 15 hours at 160°–170° lost 0.1603 gram.

0.2247 gram anhydrous salt gave 0.0946 gram Na_2SO_4.

	Calculated for $C_7H_8NaNSO_5 + 1\frac{1}{2}H_2O$.	Found.
H_2O	10.16	10.63
Na	9.62	9.48

Silver Salt.—The silver salt was prepared in the usual manner, from the neutral ammonium salt. It separates from water solution at first as a white, non-crystalline compound, later in needles. After crystallizing a number of times it was analyzed.

0.2106 gram of the salt, dried at 110°, gave 0.0708 gram Ag.

Calculated for $C_7H_8AgSO_5$.	Found.
33.33	33.61

If the salt is heated, it begins to turn brown at 220°, becomes darker as the temperature is raised, and slowly decomposes without melting.

The fusion of orthomethoxysulphaminebenzoic acid with caustic potash, giving no clue to the position of the sulphamine group, the action of hydrochloric acid upon it was next studied. 0.7 gram was heated with 8–10 cc. of strong hydrochloric acid in a sealed tube at 150°–160° for three hours. On opening the tube considerable pressure was observed and the solution contained large, needle-shaped crystals. The hydrochloric acid was evaporated off, the solution extracted with ether, and the ether dried with calcic chloride. On evaporating off the ether, crystals of pure salicylic acid were obtained, as shown by their melting-point, form of crystals, and coloration with ferric chloride.

JOHNS HOPKINS UNIVERSITY,
June, 1896.

A SIMPLE AND EFFICIENT BOILING-POINT APPARATUS FOR USE WITH LOW- AND WITH HIGH-BOILING SOLVENTS.

By Harry C. Jones.

The best methods that have thus far been devised for determining the rise in the boiling-point of a solvent, caused by the presence of a dissolved substance, are not free from objections, both theoretical and practical. Some of these, apparently, cannot be eliminated, while others can be overcome to a greater or less extent.

The boiling-point method is not capable of that degree of accuracy to which the freezing-point method has been developed by Loomis[1] and myself,[2] for several reasons. Some of these have been pointed out with admirable clearness by Hite.[3] The boiling method is very sensitive to barometric changes. In this method the vapor escapes quickly from the solution in which its presence is necessary to establish the temperature equilibrium.

To these the following should be added: The difference in temperature between the liquid and surrounding objects is generally much greater in this method than in the freezing-point method, so that greater precautions are necessary to protect the solution and thermometer from changes in the temperature of external objects. In this method a part of the comparatively pure solvent is constantly separating from the solution as vapor, and is returned as a liquid, at a temperature much lower than that of the boiling solution. The amount of this liquid cannot, for given conditions, be determined with the same degree of accuracy as was possible in ascertaining the amount of ice which separated in the freezing liquid.[4] It is well known that the large Beckmann thermometers are much more liable to undergo change at the comparatively high temperatures to which it is necessary to subject them in this method, than in the freezing method, where the temperature of the thermometer is at no time very widely removed from the ordinary. For such reasons, it has been possible, hitherto, to apply the boiling-point

[1] Ber. d. chem. Ges., **26**, 797; Phys. Rev., **1**, 199.

[2] Ztschr. phys. Chem., **11**, 532.

[3] This Journal, **17**, 507.

[4] Ztschr. phys. Chem., **12**, 624.

method only to the determination of the molecular weights of substances in solution. With the aid of the apparatus here described, we have already extended its application to the measurement of the electrolytic dissociation of solutions in ethyl alcohol, and work with this and other solvents is now in progress in this laboratory. As a measure of dissociation it will thus supplement the freezing-point method, which, as I have shown,[1] lends itself so well to water solutions.

Although the boiling-point method possesses certain inherent points of weakness, yet a study of all the methods thus far proposed for carrying out such measurements, will show that in no single case has sufficient precaution been taken to remove all the possible sources of error, and, at the same time, to devise a form of apparatus simple enough to be well adapted to general practical use in the laboratory. This conclusion will be confirmed by an attempt to apply any form thus far suggested, to general use.

The following two points are to be urged against the methods now available, each being capable of producing serious error:

1. In no well-known form of apparatus thus far described has sufficient attention been given to the *effect of radiation of heat directly from the bulb of the thermometer outward upon the colder surrounding objects.* Where the apparatus is made entirely of glass, as is true of one of the best forms, judged by the results, proposed by Beckmann,[2] and also of his latest modification,[3] this point applies with special force, since neither the glass nor its liquid contents can cut off sufficiently the long heat-rays. Even when the inner tube is surrounded by a porcelain[4] or metallic jacket, containing the boiling solvent, there is no guarantee that the walls of this outer vessel are at the same temperature as the thermometer, since the two vessels are separated by a space through which the air can circulate freely. Much greater still is this source of error liable to be, when the inner vessel, in which the thermometer is placed, is simply surrounded by a jacket of asbestos, as in the apparatus of Orndorff and Cameron,[5] or that of

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[1] Ztschr. phys. Chem., **12**, 624; Phil. Mag., **36**, 465.

[2] *Ibid*, **8**, 224.

[3] *Ibid*, **21**, 246.

[4] *Ibid*, **15**, 663.

[5] This Journal, **17**, 517.

Sakurai;[1] the innermost layer of the asbestos receives heat from the boiling solution within, and also from the flame beneath, so that its temperature must be considerably higher than that of the thermometer itself.

That the effect of radiation cannot safely be disregarded can be shown experimentally by allowing the thermometer to come to the point of equilibrium in a boiling-point apparatus constructed entirely of glass, in a cool, dark room; then, keeping all other conditions constant and admitting the sunlight, a change will be noticed on the instrument. Where a method, even though it be a differential one, is thus dependent upon external conditions, it is clear that some precaution must be taken to eliminate this source of uncertainty. On the other hand, Raoult[2] has shown experimentally that the effect of radiation is negligible in the freezing-point method, which is just what one would expect, since here the difference in temperature between the thermometer and the surrounding metallic-bath containing the freezing-mixture, is at most only a few degrees.

2. An objection which applies to all the practicable forms, with that of Hite[3] and Sakurai[4] excepted, is, that *the condensed solvent is returned directly into the boiling liquid or solution in which the thermometer is immersed.* The thermometer can, therefore, never acquire the true temperature of equilibrium between the liquid and vapor phases, but must always come to rest at some point below this. This source of error has, however, been satisfactorily met in a form of apparatus constructed in this laboratory by Mr. Hite,[5] which is further removed from theoretical objections, and, for low-boiling solvents, has been shown by him to yield better results than any form thus far devised. It was, however, stated by the author that this apparatus "does not work with some heavy high-boiling liquids, probably on account of the great difference in temperature of the flask and surrounding air," his apparatus not being jacketed on the outside to prevent loss in heat by conduction.

[1] J. Chem. Soc., **61**, 989.

[2] Revue Scientifique (Paris), 1894, **2**, 321.

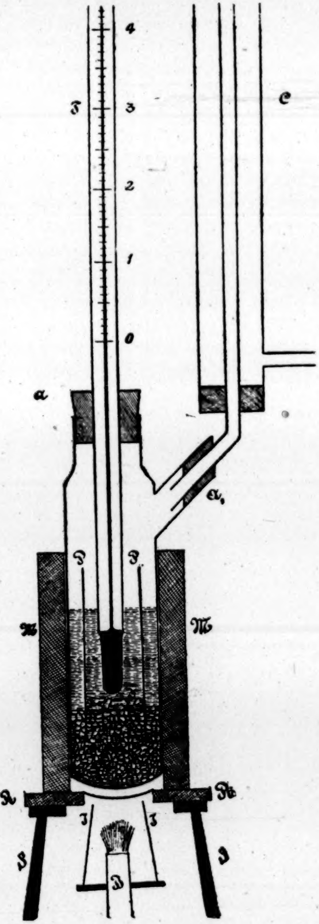
[3] This JOURNAL, **17**, 507.

[4] *Loc. cit.*

[5] *Loc. cit.*

Since this apparatus overcame so successfully, for the first time, the objection that the cold solvent is returned into the liquid in which the thermometer is placed, before it becomes heated again to the boiling-point, it seemed very desirable that it should be adapted to high- as well as to low-boiling solvents. It was with this object in mind that I began this work. The plan at first was to lengthen the Hite apparatus, jacket it on the outer side with a thick layer of asbestos to diminish the loss of heat by conduction into the cooler air, and then to jacket the outer side of the inner glass tube with a cylinder of thin platinum foil, which would be at very nearly the same temperature as the thermometer itself, and would therefore reduce the effect of radiation to a minimum. In the apparatus as first constructed, the inner glass tube was partly closed at the bottom, exactly as recommended by Hite, by means of a convex glass stopper, into whose edges notches had been filed to allow the passage of the vapor into the tube, which would establish the desired equilibrium in, and stir the liquid just around, the bulb of the thermometer. This was found to work very well with low-boiling solvents, but, like the form originally devised by Hite, it would not give satisfactory results with solvents whose boiling-points were above 100°. From some observations of my own it seems probable that this is due to the fact that the vapor under these conditions cannot enter the inner tube rapidly enough to prevent the liquid around the bulb from becoming superheated.

In the course of the work it occurred to me that it might be possible entirely to abandon the inner, glass tube in the Hite apparatus, using in its place simply the cylinder of platinum foil. This would both reduce the effect of radiation and prevent the condensed solvent from coming in contact with the thermometer until it was again reheated. It would, further, give better contact below between the liquid on the inner and on the outer side of the cylinder, than in the Hite form, and thus diminish the tendency of the solution on the inner side to become more concentrated than that on the outer. It would also allow the vapor to pass much more freely into the solution around the thermometer, and thus tend to prevent it from becoming superheated.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B

The Apparatus.

The form of apparatus which I finally devised and used, is shown in section in the figure, which is drawn approximately to scale. A is a glass tube 18 cm. high and 4 cm. in diameter. At the top it is drawn out to a diameter of about $2\frac{3}{4}$ cm. and ground to receive a ground-glass stopper. This tube is filled to a depth of from 3 to 4 cm. with glass beads. P is a cylinder of platinum 8 cm. high and $2\frac{1}{2}$ cm. in width, made by rolling up a piece of platinum foil, and fastening it in position by wrapping it near the top and bottom with platinum wire. It would be still better if the edges of the cylinder were closed tightly by welding, so that none of the liquid could pass through from one side to the other. A cylinder of some other metal, such as copper, zinc, or silver could be employed in many cases, where they would not be acted upon by the solvent or the solution, but platinum is to be preferred because of its greater resisting-power to the action of such agents. Into the cylinder P some pieces of platinum foil are thrown. These are made by cutting foil into pieces about $\frac{3}{4}$ cm. square, bending the corners alternately up and down to prevent them from lying too closely upon one another, and serrating the edges with scissors to give a greater number of points from which the boiling can take place. The bulb of the thermometer is thus entirely surrounded by metal at very nearly its own temperature, except directly above. It was at first thought desirable to protect the bulb also from radiation upwards by forcing the thermometer through a hole cut in a circular sheet of platinum foil, which would then remain attached to the thermometer stem, and suspended just above the platinum cylinder P. But, in consideration of the comparatively small angle through which such radiation can take place, it was thought to be, under the conditions, a superfluous refinement. A condenser, C, about 40 cm. in length is attached to the tube A_1, which is 2 or $2\frac{1}{4}$ cm. in diameter, by means of a cork. When it is desired to protect the solvent from the moisture in the air, the top of the condenser-tube should be provided with a tube containing calcium chloride or phosphorus pentoxide. During an experiment the vessel, *A*, is closed above by a cork through which the Beckmann thermometer, *T*, passes. *M*, is a jacket of asbestos, 12 cm. high and 1½ cm. thick, over the top of which the rate of boiling can be observed very satisfactorily. It is constructed by bending a thin board of asbestos tightly around the tube *A*, and fixing it in place by means of copper wire. Thick asbestos paper is then wound around this until the desired thickness is reached. The apparatus is supported on a small iron tripod, *S*, 8 cm. in diameter, on which rests an asbestos ring, *R*, about 9 cm. in external diameter. A circular hole is cut in the center of this ring about 3½ cm. in diameter, and over this is placed a piece of fine, copper gauze. The source of heat is a Bunsen burner, *B*, surrounded by an ordinary metallic cone, *I*, to protect the small flame from the effect of air currents. The glass vessel, *A*, is shoved down until it comes in contact with the wire gauze. Under these conditions a very small flame suffices when low-boiling solvents are employed, and not a large flame is required when a solvent like aniline is used.

Carrying Out a Determination.

The glass beads are poured into the glass cylinder, the platinum cylinder inserted and pressed down into the beads to a distance of from ½ to 1 cm. The platinum plates are then introduced into the platinum cylinder, the end of the tube *A*, closed with a cork, and the ground-glass stopper inserted in *A*. The apparatus is then set in a small beaker-glass and weighed. The solvent is then introduced and the whole reweighed. Great care must be taken that not enough solvent is employed to boil over from one side of the platinum cylinder to the other. In case a laboratory is not provided with a balance capable of weighing accurately 200 or 300 grams, the solvent must be weighed directly and then poured into the apparatus. This, for low-boiling solvents, is necessarily less accurate than the above described method of procedure. After the solvent is weighed, the glass stopper is removed and the thermometer, fitted tightly into a cork, is placed in position, as shown in the drawing. The apparatus is then placed upon the stand in the mantle of asbestos, the cork removed from *A*, and the condenser attached. Heat is then applied and the solvent boiled. The size of the flame must be so regulated by means of a screw pinch-cock, that the boiling is quite vigorous, but not so violent as to be of an irregular or explosive character. A quiet but very active boiling is absolutely essential to the success of the experiment. The time required to establish the true temperature of equilibrium between the pure liquid solvent and its vapor is very much greater than in the case of a solution. This is strictly analogous to what is observed with the freezing-point method. Here the time necessary to establish the temperature of the equilibrium between the solid and liquid phases of the pure solvent is always much greater than for a solution. Before taking a reading on the Beckmann thermometer it is always necessary to give it a few sharp taps with a lead pencil, and indeed this should be done occasionally while the mercury is rising, and especially when it is near the point of equilibrium. The use of an electric hammer to accomplish this object is an unnecessary complication. A small hand-lens, magnifying a half dozen times, is quite sufficient to use in making the readings. It is always best to redetermine the boiling-point of the solvent. After this point has been settled, a tube containing the substance whose molecular weight it is desired to determine, pressed into pellets, is weighed, and a convenient number of these poured into the solvent, either through the condenser or directly through the tube *A*, when the solvent is not too volatile, and has ceased to boil. The tube is then reweighed, and the amount of substance introduced thus ascertained. The boiling-point of the solution is then determined.

The carrying out of a determination with a low-boiling solvent is a much easier process than with one boiling at a considerably higher temperature.

Thus, when anisol or aniline is employed, much care and some experience are necessary to determine the rate of boiling which must be adopted. If the boiling is too slow, the thermometer will never reach the temperature of equilibrium ; if so rapid that it is irregular and explosive, the thermometer may rise above the true point and then suddenly drop below it at the moment when a large amount of the vapor is evolved. In a word, for high-boiling solvents, the rate of boiling must be as vigorous as possible, in order to proceed with perfect regularity.

All the forms of apparatus thus far devised are somewhat affected by the size of the flame used, provided, always, that the flame is large enough to produce rapid, and not large enough to produce explosive boiling. This is probably due to the corresponding change in rate at which the condensed solvent is returned to the boiling liquid. If this be the true explanation, then that form of apparatus which prevents the condensed solvent from coming in contact with the thermometer until it has been reheated, should be least affected by the size of flame used, and such is the fact. The apparatus of Hite, while not quite independent of the rate at which heat is added, is yet far less affected by a change in the size of the flame than any other form. The same point applies to the apparatus here described.

In all the determinations which I have made with my apparatus the barometer was carefully watched, but after the boiling-point of the solvent had been determined, the series of measurements could be carried out so quickly, that the changes in the barometer during this short interval were so slight that they could often be neglected. Whenever they were of appreciable value a correction was introduced into the results.

The Results.

The results which I have obtained are given in the subjoined tables. After the necessary details had been worked out, *every determination made was accorded an equal value, and every result is given.* No correction is introduced for the amount of the solvent which existed in the form of vapor or was condensed on the walls of the apparatus, since this could not accurately be determined. The solvents and the compounds whose molecular weights it was desired to determine, were purified by the methods best adapted to each case, and their degree of purity ascertained either by their melting- or boiling-point. The water was removed from the ether by sodium, from the benzene by fractional crystallization. The anisol and aniline were obtained sufficiently pure by fractional distillation. The anthracene was purified by boiling for two days with ethyl acetate, filtering, washing with cold ethyl acetate, crystallizing from glacial acetic acid, and subliming.

For several of the compounds used I am indebted to gentlemen working in this laboratory. For the acetanilid, to Mr. C. E. Waters; for the triphenylmethane to Mr. E. E. Reid; and for the diphenylamine to Mr. E. S. Smith.

To illustrate the speed of which the method is capable in its application, it may be stated that all the following determinations, including the adjustment of the thermometers for each solvent, were carried out in seven days.

The molecular weights are calculated from the well-known expression:

$$M = k\frac{d}{\Delta L}.$$

M is the molecular weight to be determined.
d, the amount of the substance used.
L, the amount of the solvent employed.
Δ, the rise in the boiling-point of the solvent.
k, a constant for each solvent.

SOLVENT, ETHER: $k = 2110$; boiling-point, 34°.9 at 760 mm.

Naphthalene, 128.

First Series.

	Ether. Grams.	Naphthalene. Grams.	Rise in boiling-point.	Molecular weight.
1	57.573	1.2365	0°.357	126.9
2	"	2.5155	0°.716	128.8
3	"	3.8733	1°.110	127.9
			Mean,	127.9

Second Series.

	Ether. Grams.	Naphthalene. Grams.	Rise in boiling-point.	Molecular weight.
1	53.830	0.8820	0°.273	126.7
2	"	1.8012	0°.558	126.5
3	"	2.9792	0°.920	126.9
			Mean,	126.7

SOLVENT, ALCOHOL: $k = 1150$; boiling-point 78°.3

$$P\left\{\begin{matrix}(NC_6H_5)_2\\ NHC_6H_5\end{matrix}\right., 305.$$

	Alcohol. Grams.	Compound. Grams.	Rise in boiling-point.	Molecular weight.
1	57.805	0.8622	0°.056	306
2	"	1.3023	0°.087	298
			Mean,	302

SOLVENT, BENZENE: $k = 2670$; boiling-point 80.36 at 760 mm.

Naphthalene, 128.

First Series.

	Benzene. Grams.	Naphthalene. Grams.	Rise in boiling-point.	Molecular weight.
1	74.282	1.1178	0°.302	133.0
2	"	2.2798	0°.620	132.2
3	"	3.3608	0°.900	134.2
4	"	4.7243	1°.254	135.4
5	"	6.2973	1°.678	134.9
			Mean,	133.9

Second Series.

	Benzene. Grams.	Naphthalene. Grams.	Rise in boiling-point.	Molecular weight.
1	70.560	0.7594	0°.215	133.7
2	"	2.0548	0°.574	135.4
3	"	3.0780	0°.850	137.0
4	"	4.4790	1°.234	137.4
			Mean,	135.9

Third Series.

	Benzene. Grams.	Naphthalene. Grams.	Rise in boiling-point.	Molecular weight.
1	69.702	1.0240	0°.295	133.0
2	"	2.4527	0°.704	133.5
3	"	3.8387	1°.097	134.0
4	"	5.0807	1°.458	133.5
			Mean,	133.5

Fourth Series.

	Benzene. Grams.	Naphthalene. Grams.	Rise in boiling-point.	Molecular weight.
1	65.685	0.8175	0°.246	135.1
2	"	1.8895	0°.563	136.4
3	"	2.9787	0°.893	135.6
4	"	4.0707	1°.222	135.4
			Mean,	135.6

SOLVENT, ANISOL: $k = 4430$; boiling-point 152°.

Acetanilid, 135.

First Series.

	Anisol. Grams.	Acetanilid. Grams.	Rise in boiling-point.	Molecular weight.
1	59.210	0.6241	0°.270	173.0
2	"	1.2502	0°.538	173.9
3	"	2.2225	0°.946	175.8
4	"	2.8813	1°.220	176.7
			Mean,	174.8

Second Series.

	Anisol. Grams.	Acetanilid. Grams,	Rise in boiling-point.	Molecular weight.
1	59.872	0.6523	0°.282	171.1
2	"	1.5568	0°.676	170.4
3	"	2.1928	0°.926	175.2
4	"	3.0799	1°.270	179.4
			Mean,	174.0

Anthracene, 178.

First Series.

	Anisol. Grams.	Anthracene. Grams.	Rise in boiling-point.	Molecular weight.
1	60.298	0.7606	0°.276	202.5
2	"	1.4799	0°.530	205.1
3	"	1.8736	0°.685	201.0
			Mean,	202.9

Second Series.

	Anisol. Grams.	Anthracene. Grams.	Rise in boiling-point.	Molecular weight.
1	62.190	0.6053	0°.217	198.7
2	"	1.3279	0°.455	207.9
3	"	2.1170	0°.753	200.3
			Mean,	202.3

SOLVENT, ANILINE: $k = 3220$; boiling-point 182°.5 at 738 mm.

Triphenylmethane, 244.

First Series.

	Aniline. Grams.	Triphenyl-methane. Grams.	Rise in boiling-point.	Molecular weight.
1	60.126	0.8017	0°.180	238.6
2	"	1.6052	0°.353	243.5
3	"	2.2914	0°.496	247.4
4	"	2.9213	0°.654	239.2
			Mean,	242.2

Second Series.

	Aniline. Grams.	Triphenyl-methane. Grams.	Rise in boiling-point.	Molecular weight.
1	61.900	0.8956	0°.192	242.6
2	"	1.6312	0°.358	237.0
3	"	2.3258	0°.500	242.0
			Mean,	240.5

Diphenylamine, 169.

	Aniline. Grams.	Triphenyl-methane. Grams.	Rise in boiling-point.	Molecular weight.
1	64.220	0.7780	0°.224	174.1
2	"	1.3326	0°.391	170.9
3	"	1.7832	0°.535	167.1
			Mean,	170.7

Discussion of the Results.

Perhaps the fairest test of the efficiency of the several forms of apparatus which have been devised for carrying out the boiling-point method, is the relative accuracy of the results which have been obtained by their application.

The molecular weight of naphthalene in ether was worked out by Hite with his apparatus, in a series of seven determinations, ~~using~~ different concentrations of the solutions. His values vary from 128.9 to 130.8,[1] with a mean of 129.7.

The compound used with alcohol as a solvent was furnished by Dr. Gilpin, who desired that its molecular weight should be determined.

I regret that Mr. Hite did not bring under his investigation the determination of the molecular weight of naphthalene in benzene. Such determinations were, however, made by Orndorff and Cameron[2] in their apparatus. But since they have not taken the proper precautions either to reduce the effect of radiation to a minimum, or to prevent the cold solvent from coming in contact with their thermometer, their results are necessarily affected by uncertain and indeterminate errors. This is confirmed by a study of their results, which in many cases do not, for the same substance under the same conditions, agree at all satisfactorily with one another, and in a few instances such discrepancies amount to from 10 to 15 per cent.

Their determinations of the molecular weight of naphthalene in benzene agree, however, satisfactorily with one another, ranging from 141 to 145, with a mean of 143. Since my first series gave a value which was considerably lower, (133.9) I made a second, a third, and a fourth ; in all, 17 measurements. The minimum value obtained was 132.2, the maximum 137.4, with a mean of the average values of the four series of 134.7.

As high-boiling solvents, anisol and aniline were chosen. Anisol is particularly interesting because it seems to effect a certain amount of polymerization of some substances when dissolved in it. Aniline, on the other hand, from the work of Beckmann,[1] does not, and is a good example of an easily obtainable high-boiling solvent, in which the experimental result should agree with the simplest, theoretical molecular weight.

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[1] A typographical error makes this value appear to be 138.8.

[2] *Loc. cit.*

[3] Ztschr. phys. Chem., 8, 226.

Orndorff and Cameron[1] have made three series of measurements of the molecular weight of acetanilid in anisol, with the following results:

I series, max. value 145, min. value 133, mean value 139.
II " " " 166, " " 147, " " 157.
III " " " 166, " " 148, " " 157.

It is difficult to see what conclusion can be drawn from such data, other than that there is probably a certain amount of polymerization of the anilide molecules, and even this conclusion depends upon which series of results is chosen. My own measurements in this case, be they right or wrong, have at least this merit, that they agree with one another as closely as could be expected. The results obtained by Orndorff and Cameron for anthracene in anisol are not more satisfactory than the last named. Here again they made three series of measurements:

I series, max. value 200, min. value 175, mean value 194.
II " " " 200, " " 168, " " 185.
III " " " 184, " " 176, " " 179.

The values which I have found for anthracene in anisol, ranging from 198.7 to 207.9, show, as they do with acetanilide, that there is, unmistakably, a considerable molecular condensation effected in the presence of this solvent.

The determinations in aniline as a solvent are directly comparable with those of Beckmann,[2] indeed, with the results of two modifications of his apparatus. The comparatively complex form described by him in 1891,[3] involving the glass jacket containing the same solvent, gave, as would be expected, better results than the simpler device described in 1896.[4] A series of determinations of the molecular weight of triphenylmethane in aniline, gave Beckmann values in his more complex apparatus, ranging from 246 to 252, mean 249; in his simpler, from 218 to 245, mean 233. The molecular weight of diphenylamine in aniline, as obtained by Beckmann in his more complex form, ranged from 169 to 170, in his simpler, from 164 to 173.

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[1] *Loc. cit.*

[2] Ztschr. phys. Chem., **8**, 226.

[3] *Ibid.*

[4] *Ibid*, **21**, 246.

The result of these comparisons shows that the simpler apparatus here described is capable of yielding as good results for low-boiling solvents as the form devised by Hite, and at least as satisfactory for high-boiling as the best form suggested by Beckmann, which is far more complex.

The objection of comparative complexity holds also with respect to the apparatus of Sakurai,[1] with which its inventor was able to obtain fairly satisfactory results. But since its application involves the subsequent analysis of each solution used, it can plainly never come into general laboratory practice, now that we have methods which are so much simpler and more direct.

The apparatus recently described by Beckmann,[2] to whom we are as much indebted for the experimental development of the boiling-point method as we are to Raoult for its theoretical, is much simpler than some of the forms which he proposed at an earlier date. The vapor jacket is abandoned for one of hot air, which is heated directly by the flame below, and is therefore not at the same temperature as the solution which it surrounds. The author naturally gives preference to the form in which the boiling liquid is surrounded by its own vapor at the boiling temperature.

Of the various forms of vapor jackets which have been devised, none of them seem to be entirely satisfactory. The first used was constructed of glass;[3] then this was abandoned in favor of metal, and this in turn by Beckmann for porcelain.[4] Recently objections have been raised by Fuchs[5] to the porcelain jacket. He has abandoned it, in turn, in favor of metal.[6]

When a metallic cylinder, such as I have described, is used by placing it within the boiling liquid itself, and metal is also placed beneath the bulb of the thermometer, at the same, or very nearly the same, temperature as the bulb, (which is the only safe method of preventing error from radiation), *the use of either a vapor or an air jacket is entirely superfluous.* Under these conditions, a thick roll of asbestos paper, which can be made in ten minutes and will last for months, answers every purpose.

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[1] *Loc. cit.* [2] *Loc. cit.* [3] *Loc. cit.*

[4] Ztschr. phys. Chem., **15**, 662. [5] *Ibid*, **22**, 72.

[6] It is impossible to judge of the relative merits of the apparatus described by Fuchs, since his paper is not accompanied by the experimental data necessary to test its value. But from its comparative complexity, it seems quite safe to predict that it will never find general application in the laboratory.

Conclusion.

The advantages claimed for the apparatus here described are:

1. It reduces the effect of radiation to a minimum.
2. It prevents the cold solvent from coming in contact with the thermometer until it has been reheated.
3. It renders entirely unnecessary the use of a vapor mantle on the outside of the boiling liquid, a simple jacket of asbestos, under these conditions, answering every purpose.
4. It is simpler, more easily constructed, and less difficult to manipulate, than any form thus far devised that is capable of giving results which are even fairly satisfactory.
5. It thus seems to meet the theoretical obligations of the method more nearly than any other form. That it meets the practical demands is shown by the results.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
April, 1897.

ALUMINUM ALCOHOLATES.

BY H. W. HILLYER.

In a former paper[1] we detailed the results of a research in regard to the action of aluminum on ethyl alcohol to which a small amount of fuming stannic chloride had been added. Since sending that paper to the publisher, other observations have been made, which add somewhat to our knowledge of this reaction; and similar studies have been made with methyl alcohol and the two propyl alcohols.

As stated in the article referred to, various anhydrous chlorides, which are soluble in alcohol, were used in an attempt to avoid a difficulty encountered in using mercuric chloride. When absolute alcohol is poured upon chipped aluminum and either platinic chloride, mercuric chloride, or stannic chloride is then added, a rapid deposition of the metal is soon noticed and then, with rise in temperature, an increasing evolution of hydrogen followed by a slower evolution, which is long continued, even on application of external heat. A large amount of aluminum is dissolved, enough, in some cases, to make the solution pasty or even solid with the product of the reaction. It has been found that sublimed ferric chloride will also, to a slight degree, bring about the action of aluminum on alcohol, and that even aluminum chloride produces a slight evolution of hydrogen when the chloride is freshly prepared by action of dry hydrochloric acid on metallic aluminum. External application of heat is necessary to the progress of any considerable reaction in the case of ferric chloride or aluminum chloride.

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[1] This JOURNAL, 19, 37.

By passing dry hydrochloric acid gas into absolute alcohol standing over chipped aluminum, the metal is readily dissolved with evolution of hydrogen and development of heat. So much aluminum may dissolve in this way that on allowing the solution to cool it becomes solid by separation of a crystalline compound—probably an addition-product of alcohol and aluminum chloride. If, instead of passing into the alcohol a continuous stream of hydrochloric acid gas, a small amount of an alcoholic solution of the gas is added to the alcohol, the action is slower to begin, but increases in vigor till its rate is quite comparable with that induced by the use of anhydrous chlorides of the metals. This form of the reaction is very nicely shown by letting hydrochloric acid gas bubble into the alcohol standing over the chipped aluminum, but removing the gas delivery tube as soon as a fairly rapid evolution of hydrogen is noticed. The reaction will then continue at a good rate, if the mixture is slightly heated occasionally, for more than an hour, until enough aluminum has dissolved to make a jelly when mixed with an equal quantity of water. This hydroxide or basic chloride is, however, entirely soluble in a large quantity of water.

In all the cases noted, aluminum chloride has been added, or the conditions were such that it could be formed by decomposition of the hydrochloric acid or anhydrous chloride present. In the case of some of the alcohols, it was found when the stannic chloride was dissolved in a small portion of alcohol, and this solution then added to the main portion of the alcohol, that the action on the aluminum was more vigorous than when the same amount of the chloride was added to the whole of the alcohol. To explain this, it seems to us that in adding the stannic chloride to the smaller quantity of alcohol, the temperature was raised high enough to cause the formation of an addition-product of the alcohol and stannic chloride, and that it was upon this compound that the aluminum acted first, and that later it acted on an addition-product of the alcohol with the aluminum chloride which had been found. It is known that all of the anhydrous chlorides used form addition-products with common alcohol. Such addition-products are also known with other alcohols, and it may be said that we obtained a crystalline compound by action of stannic chloride on isopropyl alcohol—probably $SnCl_4 : 3C_3H_7OH$, as shown by analysis.

For a rapid and satisfactory solution of the aluminum, it may be desirable to have a "couple" of the more easily reducible metals and the aluminum, though our later experiments with hydrochloric acid gas seem to show that it isn ot necessary.

With the reactions involving the use of stannic chloride and hydrochloric acid gas, it is also necessary to have complete dehydration. When the reaction is in full career, the addition of a little water will nearly or entirely stop the action. In this respect there is another marked contrast with the reactions involving mercuric chloride where the presence of water seems to work no harm.

The observations made would then seem to show that, in general, it is necessary to a satisfactory action of aluminum on alcohol: that it should be anhydrous, that it should contain an anhydrous chloride with which it can form an addition-product, and that the aluminum should be coupled with a more easily reducible metal.

Aluminum Methylate.—The methyl alcohol used was dehydrated by anhydrous copper sulphate and subsequently distilled. Aluminum acts on methyl alcohol under conditions similar to those favorable to its action on common alcohol. On driving off the excess of alcohol a gelatinous mass remains, but on attempting to distil under diminished pressure, the mass does not fuse, but simply crumbles to a black powder and yields no condensable distillate. Only two reactions suggest themselves for the action of aluminum on methyl alcohol. They are expressed by the following equations:

$$2Al + 6CH_3OH = 2Al(OH)_3 + 3C_2H_6.$$
$$2Al + 6CH_3OH = 2Al(OCH)_3 + 3H_2.$$

It was found that the evolved gases, passed through sulphuric acid to retain the alcohol, when mixed with air, exploded violently and gave no indication of the presence of carbon dioxide when clear lime-water was added to the gaseous residue after the explosion, thus showing the presence of hydrogen only. From this the second equation seems the more probable during the first part of the reaction at least. At a later stage it might be that the nascent hydrogen acted on the methylate previously formed and changed it to the hydroxide, as indicated by the equation:

$$Al(OCH_3)_3 + 3H_2 = Al(OH)_3 + 3CH_4.$$

The following experiments show, however, that this is not the case.

In some cases, if not every case, the aluminum alcoholates are soluble in the alcohol from which they are derived. With this thought in mind, an attempt was made to determine whether aluminum methylate had really been formed, and decomposed on heating, or aluminum hydroxide had been the final product of the reaction of the aluminum on the alcohol. After a completion of a reaction with aluminum, methyl alcohol and stannic chloride, a large excess of methyl alcohol was added, and the whole allowed to stand over night. The liquid was decanted from an insoluble residue, and filtered out of contact with the air. In measured quantities of this solution, the aluminum and the chlorine were determined to ascertain how much of the aluminum could be accounted for as chloride. 10 cc. of the filtrate were diluted with water, acidified with hydrochloric acid, and the aluminum precipitated by ammonia. From this hydroxide 0.2245 gram of aluminum oxide were obtained, equivalent to 0.1189 gram of aluminum. To determine the chlorine, 10 cc. of the same solution were diluted with water, acidified with nitric acid, and brought to boiling. On adding silver nitrate a precipitate was formed, but it required persistent and very careful filtration to bring the filtrate to final clearness. The reason for this difficulty in clearing, and the cause of the failure of the silver chloride to become curdy has not yet been found. The silver chloride formed weighed 0.4113 gram, equivalent to 0.0897 gram of chlorine, an amount corresponding to 0.025 gram of aluminum as chloride.

Considering the similarity of the reaction with this alcohol to those of the other alcohols, and the fact of the evolution of hydrogen during the reaction rather than a hydrocarbon, the presence of aluminum in solution in a form not the chloride can be most easily explained on the supposition that the reaction is normal, that aluminum methylate is formed, but that it is decomposed on attempting to distil it.

Aluminum Propylate.—The normal propyl alcohol used in these experiments was dehydrated by anhydrous copper sulphate. It boils at 97°. In carrying out one of our experiments, 10 grams of aluminum and 150 cc. of alcohol were placed in a retort and then 2 cc. of fuming stannic chloride were slowly added. No perceptible effect was produced. On applying heat a slight evolution of gas occurred, but ceased on removing the source of heat. On adding 1 cc. of the chloride, an evolution of gas commenced, which was slow at first, but soon became so violent that external cooling was necessary to prevent boiling over. After this spontaneous action became weak, external heating induced further action, which continued several hours until the mass in the retort became quite viscous. In a subsequent experiment approximately the same amounts of aluminum and of alcohol were used, but instead of adding the chloride directly to the whole amount of the alcohol, it was first dissolved in a small quantity of the alcohol and then added. 5 cc. of stannic chloride were dissolved in 10 cc. propyl alcohol, and of this solution 2½ cc. were slowly added to the main bulk of the alcohol already standing on the chipped aluminum. Action did not become noticeable for about ten minutes, but then tin began to be deposited; a slow evolution of hydrogen was noticed, which rapidly increased, and soon became violent, as before.

The subsequent treatment of the product of reaction was similar to that used with the ethylate. The second of the two operations described above gave a much larger yield of the propylate on distilling, and it showed less indication of the presence of aluminum chloride by fumes at the commencement of the distillation. When the products were redistilled at a low pressure, they gave an amber-colored distillate, sometimes solidifying to a clear mass, which gradually became opaque, and sometimes immediately solidified to an opaque solid of the appearance and consistency of fresh commercial grape-sugar. By fractionating, a product was obtained melting at 65° and boiling under 15 mm. pressure between 235° and 255°. The first fractions were more yellow than the last fraction, which boiled with approximate constancy at 255°. The aluminum in the part boiling at 255° was determined by dissolving in nitric acid, heating the solution till oxidation was no more apparent, evaporating and igniting the residue. An amount of oxide, Al_2O_3, was left, which indicated 14.3 per cent. of aluminum. By dissolving in hydrochloric acid and precipitating with ammonia, the percentage of aluminum found was 13.2. There should be in aluminum propylate 13.1 per cent. of aluminum. The product, made by another operation and distilling between 257° and 262° at 20 mm. pressure, was analyzed by combustion. In order to protect it from the moisture of the air, it was melted and drawn into weighed glass bulbs with capillary ends, and these, after cleaning and weighing, were dropped into the combustion-tube. The combustion gave:

	Per cent.
H	10.4
C	53.4

The theory requires:

	Per cent.
H	10.2
C	52.9

Aluminum Isopropylate.—Isopropyl alcohol is acted on by aluminum in presence of stannic chloride with evolution of hydrogen under conditions like those used for the normal alcohol, but with less apparent readiness. On heating the product under diminised pressure, however, no distillation takes place, but a decomposition like that observed with methyl alcohol.

Amyl alcohol yields a volatile aluminum compound, of a yellow color, and boiling at 291° C. under a pressure of 12 mm.

By the use of aluminum as a reducing-agent, and stannic chloride, platinic chloride, or mercuric chloride as the sensitizing-agent, there seems no doubt that reduction may be performed in entire absence of water, when the substance to be reduced can be dissolved in any of the alcohols, in benzene, ether, or any solvent with which alcohol will mix when it is added to evolve hydrogen with the sensitized aluminum. From later experiments it is doubtful whether the presence of the precipitated tin, platinum or mercury, is essential. Commercial aluminum at least, containing slight impurities of carbon and iron, evolves hydrogen quite freely under the conditions indicated above, by starting the action with hydrochloric acid.

I wish to express here my hearty thanks to Mr. O. E. Crooker, and especially to Mr. R. F. Hastreiter, by whom much of the experimental work detailed above has been done in connection with graduating theses in this laboratory.

LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF WISCONSIN,
MAY 1, 1897.

BEHAVIOR OF CHLORAL HYDRATE WITH AMMONIUM SULPHIDE.

BY JOSEPH LESINSKY AND CHARLES GUNDLICH.

While studying the reactions of chloral hydrate, we observed that when dissolved in water and mixed with a little ammonium sulphide, it threw down a precipitate only after a certain time had elapsed. This precipitate separated out almost instantaneously after a certain number of seconds had been counted. Upon further experiment we found that, if the concentrations are the same, the precipitate will appear, every time the experiment is tried, in exactly the same number of seconds, provided the temperature is the same.

At first we had considerable difficulty in repeating the experiment, as we had prepared a fresh quantity of ammonium sulphide. It was found, however, that this did not react with the chloral hydrate, even after standing a long time. We were more successful on using a well saturated solution of ammonium sulphide, and especially a solution that had been standing for several days, in other words, a solution of the polysulphides.

To show this reaction, the following conditions were observed:

Two grams of chloral hydrate were dissolved in 25 cc. of water, 10 cc. of this solution run out of a burette into a narrow beaker, and 5 cc. of yellow ammonium sulphide poured in, not run in. The liquids must be mixed as quickly as possible. It is best to shake the mixture slightly, and allow it to stand on a piece of white paper, so that the sudden appearance of the precipitate can be seen from a distance in showing the experiment.

At different temperatures the reaction is retarded or hastened, the time necessary for the precipitate to form being inversely proportional to the temperature and concentration.

At 1° C. the separation took place in 44 seconds.
" 20° C. " " " " " 19 "
" 45° C. " " " " " 8 "
" 65° C. " " " " " 3 "

For every 20° rise we have a gradual decrease in time.

The difference between 45° and 65° being 5 seconds.
" " " 45° " 20° " 10 "
" " " 20° " 1° " 20 "

The best way to show this reaction is to start a metronome ticking, mix the two solutions quickly and, while observing the mixture, count the number of seconds it takes before the precipitate appears. The exact nature of this reaction is not understood, especially as the resulting precipitate is evidently a mixture of sulphur and, perhaps, some sulphur compound of a mercaptan character, the odor being very characteristic. The precipitate was filtered off, and the solution, which was red, extracted with ether, the resulting oil emitting a very powerful odor and, when diluted with water, suggesting the odor of walnuts. If the concentrations of the two substances are changed, the resulting precipitate will vary in appearance. In our first experiments the precipitate was of a pinkish color, and the solution red; on heating a little on the water-bath, the precipitate became yellow and then brown, a remarkable succession of changes in color being observed. In the above mentioned experiments the precipitate was yellowish-brown in color, the solution itself being yellow, and on warming the precipitate, the color became almost black.

In order to obtain the pink precipitate, it is advisable to use an excess of chloral hydrate, but it requires some experimenting to obtain the conditions favorable for the formation of the precipitate.

Perhaps these reactions may be of value in the examination of chloral hydrate as to its purity. It is our intention to study the same, and also to determine the nature of the precipitate, and the cause of the "retarded precipitation."

There are only two such cases of retarded precipitation known to us, besides the one described by us, and, even in those cases, it has been impossible to ascertain the causes, although the reactions are not complicated, as in the case with the one described by us.

The reactions are as follows:

1. The action of sodium thiosulphate upon hydrochloric acid:

$$H_2S_2O_3 + \text{acid} = H_2O + SO_2 + S.$$

Here the sulphur separates out suddenly after a lapse of time.

2. The action of hydriodic acid with a starch solution when sulphuric acid is added:

$$2HI + H_2SO_4 + \text{starch solution} = 2H_2O + SO_2 + I_2, \text{ or}$$

$$2HIO_3 + 5SO_2 + 4H_2O = 5H_2SO_4 + I_2.$$

The last reaction is the most characteristic of the three, the iodine separating out so suddenly that most accurate results can be obtained in measuring the time. We have furthermore succeeded in procuring the same results by employing butyl chloral (croton chloral) instead of chloral hydrate, the resulting precipitate being of a beautiful lemon-yellow color. This last reaction is not as striking as the others, the precipitate requiring 2 or 3 seconds for complete separation.

NEW YORK COLLEGE OF PHARMACY,
NEW YORK, MAY 2, 1897.

A NEW AND RAPID METHOD FOR THE QUALITATIVE SEPARATION OF IRON, ALUMINIUM, CHROMIUM, MANGANESE, ZINC, NICKEL, AND COBALT.

BY ALEXANDER RAMSAY CUSHMAN.

Add ammonium chloride, ammonia to alkaline reaction, and then ammonium sulphide in slight excess. Warm and filter. Wash the precipitate and remove from the filter while still moist. Warm with moderately dilute hydrochloric acid in a porcelain dish. Complete solution of the precipitate shows the absence of nickel and cobalt. If a black residue remains, one or both are present, in which case add *aqua regia*, and warm gently until dissolved. Expel excess of acid and free chlorine by evaporation, and then make the solution strongly alkaline with ammonia, after previously adding ammonium chloride in case the amount of hydrochloric acid used upon the sulphides was small. Add bromine solution in excess, and allow to stand a few minutes. Filter and wash. The table given below shows the course of the analysis after this point is reached :

Precipitate 1.—Fe_2O_3, $MnO_2.H_2O$, $Al_2(OH)_6$, $Cr_2(OH)_6$. Remove from the filter and add KOH in excess, then Br solution and filter.	**Filtrate 1.**—$ZnCl.2NH_4Cl$, $NiCl_2.NH_4Cl$, $[Cl.Co(NH_3)_5]Cl_2$. Add KOH in large excess, allow to stand a few minutes and filter.		
Residue 2.—Fe_2O_3, $MnO_2.H_2O$. Divide in 2 parts. *Part 1.* Dissolve in HCl, add a few drops of NH_4CNS. Blood-red color shows $Fe_2(CNS)_6$ and proves Fe. *Part 2.* Fuse with $Na_2CO_3 + NaNO_3$ in O. F. of blowpipe. Bluish-green mass proves Mn.	**Filtrate 2.**—$K_2Al_2O_4$, K_2CrO_4. Divide in 2 parts. *Part 1.* Acidify with HCl, add excess of $(NH_4)_2CO_3$ and boil. A white flocculent precipitate shows $Al_2(OH)_6$ and proves Al. *Part 2.* Acidify with $HC_2H_3O_2$ and add $Pb(C_2H_3O_2)_2$. A yellow precipitate shows $PbCrO_4$ and proves Cr.	**Precipitate 3.**—$Ni(OH)_2$. (Greenish-white). Confirm in salt of phosphorus bead in the R. F. of the blowpipe. Yellow bead, cold, proves Ni.	**Filtrate 3.**—$[Cl.Co(NH_3)_5]Cl_2$, K_2O, ZnO. Heat to boiling and filter.
		Precipitate 4.—$Co(OH)_3$. Confirm in borax bead, in the O. F. of the blow-pipe. Blue bead proves Co.	**Filtrate 4.**—Acidify with $HC_2H_3O_2$, and saturate with H_2S. A white, flocculent precipitate shows ZnS. Confirm by ignition with $Co(NO_3)_2$ on charcoal. Yellow-green mass proves Zn.

REVIEWS.

A RESUME OF PROGRESS IN THE CHEMISTRY OF THE CARBOHYDRATES DURING 1896.

Activity in this field has been unabated during the past year, and it becomes more and more evident to the student of the carbohydrates that these bodies present opportunities for the study and illustration of chemical theories in no way exceeded by their very great practical and technical importance. The following review is intended to include all of the publications appearing in the chemical journals during the year, although the practical impossibility of making the record complete is fully recognized. Purely technical papers have for obvious reasons not been included. The classification employed in former years has been retained.

General Reactions.—The continued study and development of new reactions among the carbohydrates has been so fruitful that these bodies may now be fairly regarded as among the most reactive of the general classes of carbon compounds. A large number of characteristic reactions have now been well studied, involving the general principles of polymerization, condensation, oxidation, reduction, ether, and ester formations, etc. Contrary to the former view that the carbohydrates were extremely unstable and sensitive compounds, it now appears that they are capable of undergoing the most manifold changes, not alone as regards their chemical features but in their physical properties as well. Indeed in this latter field it appears that the sugars offer the best known examples for the illustration of the principles of stereochemistry, while the latest researches indicate that sugar molecules are unstable systems in which a variety of intermolecular transformations may be induced. From their nature as derivatives of polyvalent alcohols containing several hydroxyls and, according to conditions, ketone, aldehyde, or carboxyl groups, it is of course to be expected that great facility for reaction would follow.

Tollens and his pupils[1] have produced a series of condensation-products between polyvalent alcohols and formaldehyde, called *formals*. The reaction occurs readily when equal parts of the alcohol, a 40 per cent. solution of formaldehyde and hydrochloric acid of 1.19 sp. gr. are heated together. The products are crystalline and stable with the probable constitution—as illustrated by trimethylenemannite–

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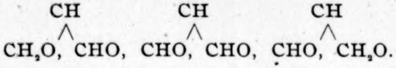
[1] Tollens, Henneberg, and Schulz: Ann. Chem. (Liebig), **289**, 20; **292**, 3; also Ztschr. Ver. Rübenzuck, Ind., 1896, 274.



$$CH_2O\overset{\overset{CH}{\wedge}}{,}\ CHO,\ CHO\overset{\overset{CH}{\wedge}}{,}\ CHO,\ CHO\overset{\overset{CH}{\wedge}}{,}\ CH_2O.$$

Sorbite also yields a triformal; adonite a diformal with one free hydroxyl; erythrite and pentaërythrite, diformals; glycerin a monoformal with a free hydroxyl, apparently in isomeric forms. Similar reaction follows with gluconic and saccharic acids.

A searching investigation upon the destructive action of more or less dilute mineral acids upon the monosaccharides, throws light upon several well-known reactions.[1] By heating dextrose, levulose, galactose, maltose, and arabinose with acids under different conditions of temperature, pressure, and time, and carefully estimating all of the decomposition-products, it was shown that the monosaccharides undergo three general phases of change which are largely independent of each other:

1. Condensation resulting in the formation of humus-like bodies.

2. Formation of levulinic and formic acids, resulting from a splitting off of a terminal carbon atom, accompanied by deoxidation of the system including the five remaining carbon atoms; a part of this oxygen goes to produce the formic acid or, under changed conditions, carbon dioxide. With the pentose sugars the result is similar. Humus-like bodies are more readily formed where the action occurs under pressure or in closed vessels. The characteristic reaction of the pentoses to yield furfurol occurs readily and, as is well known, almost quantitatively. It is interesting to note that both pentoses and furfural are endothermic compounds of almost identical degrees of heat-absorption, *viz.*, —86° and —88° calories respectively—which possibly explains the ready transition from one to the other.

3. The slow formation of carbon dioxide results in the case of the pentoses as well as in that of the hexoses.

The reaction between monovalent mercaptans and aldoses,[2] and between polyvalent mercaptans and aldehydes,[3] has now been extended to polyvalent mercaptans and aldoses.[4] The condensation occurs on heating the reacting substances in the presence of concentrated hydrochloric acid; the products are crystalline and more stable toward acids and more soluble than those with monomercaptans. Such compounds have been prepared between dextrose, galactose, mannose, xylose, and arabinose and ethylene, trimethylene, and benzoyl mercaptans.

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[1] Berthelot and André: Compt. rend., **123**, 567, 625.

[2] Fischer: Ber. d. chem. Ges., **27**, 674.

[3] Fasbender: *Ibid*, **20**, 460.

[4] W. T. Lawrence: *Ibid*, **29**, 547.

The aldose and ketose sugars form characteristic compounds with hydrazine hydrate[1] on digesting small amounts of the substances in methyl alcohol and crystallizing from ether. The constitution is supposed to be as follows:

$$CH_2OH.(CHOH)_4.CH{=}N{-}N{=}CH.(CHOH)_4.CH_2OH.$$

Such derivatives have been prepared from dextrose, fructose, and arabinose. Benzhydrazide also combines freely with aldose sugars in the presence of dilute alkalies.

Attempts have been made to utilize the properties of different hydrazines for the separation of sugars. Benzyl- and napthylhydrazine afford compounds of dextrose and fructose, which by their different solubilities permit such a separation. Methylphenylhydrazine is adapted to the isolation of galactose. Melibiose forms an insoluble compound with allylphenylhydrazine, which may be decomposed by benzaldehyde so as to free the sugar.[2] In a second paper the authors give in detail the results of their comparisons of the properties of methyl-, ethyl-, amyl-, benzyl-, and β-naphthylhydrazines of the various monosaccharides with the exception of fructose, sorbose, and mannose which form no insoluble compounds with the above.

A mixture of galactose and arabinose combines with benzhydrazide, but the arabinose derivative is insoluble and may be separated from the galactose compound. Both may then be decomposed by benzaldehyde, leaving the respective sugars free.[3]

An effort to determine the relation between configuration and lactone-formation seems not to have led to conclusive results.[4] *l*-Gluconic, *l*-gulonic, *l*-mannonic, *l*-arabonic, and α-glucoheptonic acids were studied in comparison with their stereoisomers: the gluconic and arabonic acids showed little tendency to lactone-formation but the dibasic acids were particularly active.

The theory of multirotation has received no important contribution as might have been expected to follow the announcement of Lobry de Bruyn and his associates in 1895 regarding the intramolecular transformations and changes in the optical properties of sugars under the influence of alkalies.[5] The priority of the suggestion of this cause of multirotation is claimed by von Lippmann, as recorded in his work *Chemie der Zuckerarten*, p. 130.

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[1] E. Davidis: *Ibid*, **29**, 2308.

[2] W. van Ekenstein and C. A. Lobry de Bruyn: Recueil trav. chim., **15**, 97, 225.

[3] E. Subasshow: Ztschr. Ver. Rübenzuck-Ind., 1896, 270.

[4] E. Hjelt: Ber. d. chem. Ges., **29**, 1867.

[5] *Ibid*, **20**, 3078.

It is pointed out that the supposed destruction and loss of sugar in factory-processes through the use of lead oxide or hydroxide is really due to a change in the rotary form of the sugar through the influence of the alkali.[1]

The decomposition of sugars heated with alkalies, and the appearance of brown color in such solutions is proportional to the temperature and concentration of alkali. If air is excluded no brown color results under a temperature of 45° nor is lactic acid produced, but if the solutions are boiled with free access of air the decomposition goes on more rapidly and lactic and formic acid result.[2]

New Synthetic Sugars.

Fischer has added two more to his long list of synthetic sugars by employing his already familiar methods. From xylose was obtained xylonic acid;[3] this, by heating with pyridine becomes transformed into the new stereoisomeric lyxonic acid which by reduction with sodium amalgam yielded lyxose, a new sugar belonging to the dulcite series. The author predicts its preparation by Wohl's "Abbau" method from galactose. In a similar way rhamnose was transformed through the stages of rhamnonic acid and isorhamnonic acid to isorhamnose, a methylpentose stereoisomeric with rhamnose.[4]

Monosaccharides.

Pentoses.—The qualitative reaction of the pentoses and pentosans with phloroglucin has been carefully studied.[5] On warming these substances with concentrated hydrochloric acid and phloroglucin a red color is produced which, with transmitted light, gives characteristic spectrum absorption-bands. The color separates as a sediment which may be filtered out and redissolved in alcohol, rendering the reaction much more sensitive. Other sugars give a colored solution, but no absorption-bands.

The separation of arabinose from galactose by means of the benzhydrazide reaction has already been referred to under "general reactions." Arabinose forms a compound with bromal similar to those with chloral.[6]

Rhamnose seems to be to some extent assimilable in the digestive tract, experiments showing that by healthy persons eight per cent., and by a diabetic patient sixteen per cent. of the amount administered, was excreted unchanged.[1]

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[1] C. Lobry de Bruyn and W. van Ekenstein: Recueil trav. chim., **15**, 92.

[2] F. Framm: Pflügers Archiv., **64**, 575.

[3] E. Fischer and O. Bromberg: Ber. d. chem. Ges., **29**, 581.

[4] E. Fischer and H. Herborn: *Ibid*, **29**, 1961.

[5] B. Tollens: *Ibid*, **29**, 1202.

[6] Hanriot: Compt. Rend., **122**, 1127.

By fractional crystallization different modifications of rhamnose (isodulcite) have been noted; *e. g.*, β-isodulcite $[(\alpha_{\mathrm{D}} = 10^\circ$ to $12^\circ]$ and γ-isodulcite $[(\alpha)_{\mathrm{D}} = 20^\circ]$.[2]

With reference to the formation of furfurol from pentoses and pentosans, Tollens has repeated former experiments with glucuronic acid and its derivatives.[3] By distilling the acid with hydrochloric acid of 1.06 sp. gr., from 15 to 17 per cent. of furfurol was obtained, or something less than the theoretical amount. The derivatives of the acid also yielded furfurol in large quantities.

Hexoses.—Dextrose compounds with polyvalent mercaptans, with hydrazine hydrate and alkyl hydrazines, have been referred to under "general reactions." Galactose has been prepared from a kind of gum occurring in wine.[4] Galactosamine[5] loses one-half of its ammonia when boiled with methyl alcohol, and the residue has the same composition as the "osamine" of mannose.[6] A compound between galactose and choral has been obtained which still retains the power to reduce Fehling solution, and gives a red color with orcin chloride.[7]

Molecular modifications of galactose with varying rotatory power are reported as resulting from fractional precipitation of the sugar by absolute alcohol in the presence of dilute alkalies; *e. g.*, β-galactose $[(\alpha)_{\mathrm{D}} = 81^\circ.6]$ and γ-galactose $[(\alpha)_{\mathrm{D}} = 53^\circ)$. In watery solutions these forms revert to the normal galactose.[8] A crystalline substance has been extracted from the seed of the yellow lupine, which by hydrolysis yielded galactose, but it does not appear that it was a hexavalent alcohol, although named galactite.[9] Compounds of galactose with chloral and polyvalent mercaptans have been referred to elsewhere.

Mannose has been obtained in crystalline form from a solution in absolute methyl alcohol and ether. It melts at 132°, and exhibits multirotation from $(\alpha)_{\mathrm{D}} = -13^\circ.6$ to $+14.^\circ25$.[10]

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[1] L. Lindemann and R. May: Deutsch. Archiv. f. klin. Med., **56**, 283.

[2] Tanret; Compt. Rend., **122**, 86.

[3] B. Tollens and F. Mann: Ann. Chem. (Liebig), **290**, 155.

[4] G. Niviere and A. Hubert: Rev. inter. falsific., **9**, 48.

[5] Ber. d. chem. Ges., **28**, 3082.

[6] C. Lobrey de Bruyn and F. van Leent: Recueil. trav. chim., **15**, 80.

[7] Hanriot: Compt. Rend., **122**, 1127.

[8] C. Tanret: Bull. Soc. Chim. (Paris), [3], **15**, 5.

[9] H. Ritthausen: Ber. d. chem. Ges., **29**, 896.

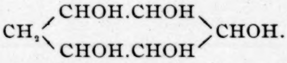
[10] W. van Ekenstein: Recueil. trav. chim., **15**, 221

The two stereoisomeric methyl-mannosides,[1] on being mixed in molecular proportions, give an optically inactive mixture. On crystallizing at a temperature of 8° or lower, the two isomers crystallized separately, and by allowing the crystallization to proceed *in vacuo*, crystals of unusual size were obtained, which could be mechanically separated. Crystallization above 15° yielded only the racemic compound. This would indicate that the racemic formation occurs under heat-absorption.[2]

The occurrence of sorbose in fermented fruit juices is now accounted for by the isolation of a microbe which exerts an oxidizing influence on sorbite. Inoculation of this microbe into solutions containing sorbite, suffices to produce sorbose.[3]

Volemite, the heptavalent alcohol identified in 1895,[4] while evidently of carbohydrate nature, does not undergo hydrolysis with sulphuric acid, is non-fermentable, and does not react with phenyl hydrazine, although it combines with acetyl chloride, acetic aldehyde and benzaldehyde.[5]

The true position of quercite as a carbohydrate is still doubtful.[6] By oxidation with nitric acid it yields mucic and trihydroxyglutaric acids; with permanganate, malonic acid. The latter indicates the correctness of Kannonikow's formula,



$$\mathrm{CH_2}\left\langle\begin{matrix}\mathrm{CHOH.CHOH}\\ \mathrm{CHOH.CHOH}\end{matrix}\right\rangle\mathrm{CHOH.}$$

Disaccharides.

Sucrose.—A very thorough study has been made by J. H. Long of the action of salts upon solutions of sucrose. The results of the investigation show that sucrose solutions are completely inverted by a large number of different salts. The action is slow at ordinary temperature, but increases rapidly above 60°; the action is also influenced by light. Apparently the inversion follows the general law governing the action of weak acids on sugars. Although all conditions of concentration, temperature, etc., were carefully controlled, the inversion coefficient was not constant for different salts.[7] Solutions of pure sucrose of 10 and 50 per cent. strength acted upon by sulphurous acid at temperatures from 30° to 80°, showed that inversion resulted in this case as well as with other acids in accordance with the Guldberg–Waage law. The same was found true in the presence of salts and other impurities.[1]

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[1] Ber. d. chem. Ges., **28**, 1145, 1167.

[2] E. Fischer and L. Beensch: Ber. d. chem. Ges., **29**, 2927.

[3] G. Bertrand: Compt. Rend., **122**, 900.

[4] Ber. d. chem. Ges., **28**, 1973.

[5] E. Bourquelot: J. Pharm. Chim. [26], **2**, 385.

[6] H. Kiliani and J. Schäfer: Ber. d. chem. Ges., **29**, 1762.

[7] J. H. Long: J. Am. Chem. Soc., **18**, 121, 693.

The electrical resistance of a solution of sucrose is a function of its concentration, the minimum being with a solution of a gram-molecule in something more than 10 liters of water. With a constant current the resistance is a function of the temperature, diminishing as t° increases. The current seems to produce only an inappreciable transport of sugar to the positive pole.[2]

A report on the use of Schollmeyer and Huber's electrolytic method for the purification of sugar solutions in factory operations, shows that the result is satisfactory, but that electrolysis alone cannot successfully compete with the lime process of clarification. The success of the present process is due to its combination with the lime process.[3]

The effect of basic lead acetate upon sugar solutions has been carefully studied, and a number of important conclusions drawn, mostly of technical application: among these, that the presence of basic lead acetate affects the rotation of sugar solutions, through the formation of lead compounds. In the presence of baryta, strontia or lime, lead saccharates are precipitated: magnesia is also efficient in this respect. Raffinose[4] is thrown down from aqueous solutions by very basic lead acetate.

In an address on the origin of sugar in the beet, F. Strohmer reviews in an interesting manner the physiology of the sugar-beet. The total amount of water and sugar present during the latter half of the growth of the beet is practically constant; the sugar is prepared in the leaf and its amount depends on the vigor and extent of this part of the plant. When removed from the earth the beet steadily loses sugar by the process of transpiration.[5] Sucrose is said to be formed from the starch in potatoes by freezing (see Starch).

A new method for recovering sucrose from beet-molasses has been patented by G. Kassner.[6] After treatment with lime or basic acetate of lead the filtered solution is slightly warmed, and treated with a thin paste of lead oxide or hydroxide, which precipitates the sucrose as a lead compound. One molecule of sugar requires somewhat more than two molecules of lead oxide, PbO. The lead saccharate is sufficiently insoluble to permit of washing, and is afterwards decomposed by carbon dioxide. The lead carbonate is recovered by ignition. Criticisms of this process, both pro and con, have been published.[1] It does not appear that with proper manipulation there is danger of any lead compounds remaining in the crystallized sugar.

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[1] K. Stiepel: Ztschr. Ver. Rübenzuck-Ind., 1896, 654, 746.

[2] F. von Siegroth: Elektro. Chem. Zeit., **3**, 33. [3] Baudry: *Ibid*, July 5, 1896.

[4] H. Suoboda: Ztschr. Ver. Rübenzuck-Ind., 1896, 107.

[5] F. Strohmer: Oesterr-Ung. Ztschr. Zucker-Ind. u. Landw., **25**, 589.

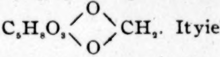
[6] G. Kassner: *Ibid*, **25**, 800.

Another patent relating to the same process involves treatment of the molasses with alkali or calcium sulphite and sulphur dioxide, and heating to boiling under pressure.[2]

Amorphous Carbohydrates.

Cellulose.—The valuable researches of Cross and Bevan and their associates upon the constitution of the celluloses is still progressing and with notable results. Reports from these authors during the past year have reference mainly to the cellulose of cereal straws. By dissolving bleached straw-cellulose in concentrated sulphuric acid, and then diluting with water, a precipitate was obtained which was practically free from substances yielding furfurol; the soluble portion retained practically all of such materials originally present in the straw. On neutralizing this solution with barium carbonate a portion of these materials was thrown down, but the solution still reduced Fehling's solution strongly; the osazone derived from it melted at 154°; analysis indicated a substance with C_{16} to C_{18}; by oxidation, acetic acid was produced, and there was evidence of the presence of hydroxyl groups capable of acetylization. The cereal straws are made up of the following constituents: Ligno-celluloses, 33 per cent.; resistant celluloses, 25 per cent.; hemicelluloses, 21 per cent.; pentosans, 21 per cent.[3]

An attempt to trace the development of the various celluloses and related substances in the growing plant (barley) has given interesting results.[4] Substances yielding furfurol were found in both the soluble and the permanent tissue, but these are localized in the cell-substances, and are generally changed into permanent tissue. In the growing plant the "furfuroids" are separated from the cellulose by 1 per cent. sulphuric acid at a pressure of three atmospheres. In the early stages of growth the "osazones" melt at 180°–190°, *i. e.*, are not pentose compounds. Up to the flowering period the products of hydrolysis are fermentable, and do not yield carbon dioxide when oxidized with hydrogen peroxide. From the flowering period on there is no constant increase of the pentosan-formal complex.

From the mature straw the portion separable by sulphuric acid has the empirical formula $C_6H_{10}O_5$, and probably the constitution of a pentosan-formal,  $C_5H_8O_3\begin{matrix}\diagup O \diagdown \\ \diagdown O \diagup\end{matrix}CH_2$. It yields the "osazones" of the pentoses after hydrolysis, is characteristically decomposed with formation of carbon dioxide, and the product of hydrolysis is partially fermentable. The authors regard the furfurol-yielding substances as direct products of assimilation.

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[1] See A. Wohl: Ztschr. Ver. Rübenzuck-Ind., 1896, 159; "C. W.," Dingler's Pol. J., **301**, 46; G. Kassner: *Ibid*, **301**, 215; Pharm. Cent. H., **37**, 4.

[2] K. Kastengren, Boehm: Ztschr. f. Zuck-Ind., **20**, 279.

[3] Cross, Bevan and Beadle: J. Am. Chem. Soc., **18**, 16.

[4] *Ibid*, p. 8; Cross and C. Smith: Chem. News, **74**, 175: Ber. d. chem. Ges., **29**, 1457.

Former experiments upon the rise in temperature of cellulose through the absorption of atmospheric moisture,[1] have been continued, the results indicating that "viscoid," a form of cellulose precipitated from solutions in alkali and carbon disulphide, behaves in this respect like finely divided cotton.[2]

Experiments upon the saccharification of sulphite-cellulose and sawdust, for the purpose of producing alcohol[3] by the fermentation of the product, showed that 0.4 to 0.6 per cent. sulphuric acid acting at eight atmospheres pressure during two hours produce 45 per cent. of sugar from sulphite-cellulose. 0.5 per cent. sulphuric acid at nine atmospheres pressure during one-fourth hour produced 22.5 per cent. sugar from sawdust. From 100 parts of sawdust, 6.5 parts of pure alcohol were obtained. A tetranitrocellulose of marked explosive properties has been prepared by the action of nitric acid on dinitrocellulose in the presence of strong dehydrating substances like sulphuric acid and phosphorus pentoxide.[4]

Certain cellulose derivatives give promise of such industrial value as to warrant the securing of patents by their originators. Cross and Bevan have patented in England and Germany a process for preparing cellulose tetracetate by heating dehydrated cellulose and zinc acetate with acetyl chloride. The product is solid, but dissolves in chloroform and resembles collodion without possessing its explosive character.

Chardonnet and Lehner have patented in Germany a method of making an imitation of silk ("Glanz-cellulose"). A description[5] states that the glistening appearance is due to the fact that the fibres are solid. It is produced by nitrating cellulose, dissolving in alcohol and ether, passing the viscous mass through fine holes, and allowing the solvent to evaporate; the fine threads are spun to yarn, and denitrated by ammonium sulphide, after which it is no longer explosive or combustible. The silk is more hygroscopic than ordinary cellulose, and less elastic, and only 70 per cent. as strong as silk.

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[1] Chem. News, **71**, 1.

[2] C. Beadle and O. Dahl: Chem. News, **73**, 180.

[3] E. Simonson: Norsk. tekniks. Tidskrift, 1895, 65.

[4] H. N. Warren: Chem. News, **74**, 239.

[5] Cross and Bevan: J. Soc. Chem. Ind., **15**, 317.

An oil and water-proof paper has been patented by E. Schering. It is prepared by saturating hydrocellulose (parchment paper) with pyroxylin.

The hemicellulose of the thickened cotyledons of seeds of lupine previously shown to yield galactose and a pentose on hydrolysis, has been studied during the process of germination and is found to be largely absorbed. It undoubtedly serves as a reserve material in the seed.[1]

Analysis of xylan carefully prepared from corn-cobs and dried by a special method, shows its composition to be represented by the formula $C_5H_8O_4$. A similar preparation from birchwood gave the formula $C_4H_6O_3$. It is suggested that this is a tetrosan and further study is reserved. Mannan from vegetable ivory has a composition represented by $C_6H_{10}O_5$.[2]

Starch.—A study of the progressive hydrolysis of starch by acids, controlled by frequent determination of rotation and reducing-power, shows a constant relation between these two properties at all stages of hydrolysis.[3] The conclusion is drawn that in any acid-converted starch-product the specific rotation represents a definite composition, and in such a product but three simple carbohydrates exist. The speed of hydrolysis follows about the same law as sucrose.

The starch of potatoes which have been frozen or kept for some time at a temperature near the freezing-point, is changed to sugar (sucrose and dextrose). If such potatoes are returned to ordinary temperature, in time some of the sugar disappears in the process of transpiration, and a large portion (about 62 per cent.) is changed back to starch.[4]

Starch paste is changed by chloroform into modifications similar to those produced by the action of acids. A solution of starch in contact with chloroform for three months no longer gave the usual reaction with iodine. By evaporating the solution and precipitating with alcohol, dextrins of varying solubility were obtained.[5]

Iodine and starch form a chemical compound, *e. g.*, starch is able to withdraw iodine from other compounds, forming iodide of starch. From the latter compound the iodine is separated by dialysis in the form of hydriodic acid.[6]

Starch exposed to a solution of chloral swells up to a nearly clear, viscous solution. After filtration such a solution gives no color reaction with solid iodine: if water be added to this solution, a blue color appears at the zone of contact with the iodine. These and other reactions show a restrictive influence of chloral on the formation of the starch-iodine compound.[1]

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[1] E. Schulze: Ztschr. phys. Chem., **21**, 392.

[2] S. W. Johnson: J. Am. Chem. Soc., **18**, 214.

[3] G. Rolfe and G. Defren: *Ibid*, **18**, 869.

[4] W. Bersch: Oesterr-Ung. Ztschr. Zuck-Ind. u. Landw., **25**, 766.

[5] F. Musset: Pharm. Centr. H., **37**, 587.

[6] *Ibid*, **37**, 556.

The isomaltose of Lintner and Düll, and others, is still regarded as of doubtful existence. Among the products of diastatic action upon starch, isomaltose is said to be formed. It is pointed out that different dextrins result, of which the so-called No. III resembles maltose, but is not easily fermented by yeast of the Saaz or Frohberg types, these properties being characteristic of isomaltose. If, however, the experiments be made *in vacuo*, this product is readily fermentable. This is explained on the principles of osmosis, fermentability being dependent upon the diffusibility of the substance through the cell-membrane. Moreover, this dextrin III, if mixed with about 20 per cent. of maltose, gives an "osazon" like that described for isomaltose. The author regards isomaltose as a mixture of maltose and certain dextrins.[2]

Isomaltose may be prepared by the action of sulphuric acid on dextrose at ordinary temperature for some months. By precipitation with alcohol and ether, about 27 per cent. of the original sugar was obtained as a product of a specific rotation of $+70^\circ$ and a reducing-power two-thirds that of dextrose. In a similar way maltose may be condensed to isomaltose.[3]

Methods of Analysis.

A careful review of all of the methods for the quantitative estimation of the pentoses and pentosans leads to the conclusion that the gravimetric precipitations of furfurol obtained by distillation of the material with hydrochloric acid of 1.06 sp. gr. with either phenyl hydrazine or phloroglucin is the most satisfactory; on some accounts the latter reagent is preferred. The weight of phenyl hydrazine precipitate $\times$ 0.9676 $=$ weight of pentosan in original material. The weight of phloroglucin precipitate divided by the factor 1.82 to 1.93 $=$ furfurol, which multiplied by 1.84 $=$ weight of pentosan in original material.[4]

A rapid and accurate method of determining the amount of copper thrown down by reducing sugars is to filter on a porcelain Gooch crucible, and ignite until the cuprous is changed to cupric oxide. Tables are given for the values of dextrose, lactose, and maltose in terms of cupric oxide.[1]

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[1] E. Schar: Pharm. Centr. H., **37**, 540.

[2] E. Prior: Centr. Bl. f. Bakt. u. Parasiten-kund., **2**, 271; also Forsch: Ber. ub. Lebensm. u. Bez. Z. Hyg., **3**, 322.

[3] H. Ost: Chem. Ztg., **20**, 761.

[4] B. Tollens, F. Mann, M. Kruger: Ztschr. angew. Chem., 1896, 33; also J. f. Landw., 1896, 171.

By adding potassium cyanide to Fehling's solution until the blue color disappears and then a measured excess of Fehling's solution, the mixture may be titrated with reducing sugars to the point where the blue color disappears and the amount of sugar calculated. This is said to be less accurate and convenient than a similar method previously suggested, involving the use of potassium ferrocyanide.[2]

By boiling a measured amount of sugar solution with an excess of Fehling's solution, the excess of the latter may be determined by adding phenyl hydrazine choride and measuring the nitrogen gas thus liberated.[3]

The removal of lead from sugar solutions clarified by means of basic lead acetate, may be accomplished by the use of ammonium oxalate. The ammonia thus freed is without effect on the determination.[4]

Ammoniacal silver nitrate is quantitatively reduced by solutions of glucose, levulose, and galactose; sucrose, starch, and dextrin are without effect, while lactose and maltose reduce irregularly, owing to continued hydrolysis by the ammonia.[5]

Since the specific rotation of levulose changes at different temperatures, this property may be turned to account for its estimation in the presence of dextrose. The rotation of a mixture of dextrose and levulose diminishes regularly from 0° to 88° at which it becomes zero. By observing the total variation, data are obtained for a formula to be employed in calculating the results of analytical observations. A special observation tube is necessary for the polarimetric readings at low temperature. It is also noted that at 0° the rotation does not become constant for some hours.[6]

Lactose may be estimated in milk by precipitating the caseïn with phenol and basic lead acetate. From the filtrate lead may be removed by sodium sulphate.[7]

If milk is clarified by boiling with basic lead acetate, sugar is destroyed. The results of polarimetric determination are usually lower than by gravimetric methods.[8]

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[1] G. Defren: J. Am. Chem. Soc., **18**, 749.

[2] A. Gerrard; Pharmzeut. J., 1895; Causse: J. pharm. Chim. (6), **3**, 433.

[3] E. Riegler: Wien. Med. Blätter, 1896, 451.

[4] Zamaron: Bull. Ass. Chim., 1895, 346.

[5] J. Henderson: Chem. News, **73**, 81.

[6] H. W. Wiley: J. Am. Chem. Soc., **18**, 81; see also Allen's Commercial Organic Analysis, Vol. I, p. 291.

[7] B. van Ketsl, Nederl, Tijdschi: Pharm., **8**, 151.

[8] E. V. Raumer and E. Spath; Ztschr. anorg. Chem., 1896, 70.

In correction of a method formerly proposed for the estimation of lactose,[1] double the normal weight of milk is taken, clarified with mercuric nitrate, diluted to 100 cc., and polarized in a 400 mm. tube. The same process is repeated with a sample diluted to 200 cc. The data thus obtained are used in calculating the true volume of liquid and the precipitate in the flask. The true polarization is found by dividing the product of the two readings by their difference.[2]

Papers on the methods of examination of honeys have appeared which, however, are too long and too technical for intelligent abstraction in this place.[3]

Acetylene gas has been found an unusually desirable illuminant for the polarimeter, giving a distinct field of view where other sources of light utterly failed.[4]

A comparison of the different methods of determining cellulose or "crude fibre" leads to the conclusion that none of the methods thus far proposed satisfies the requirements of accuracy and rapidity. With most methods the "crude fibre" still retains pentosans or oxycellulose. Others which overcome this difficulty attack the cellulose itself.[5]

Action of Ferments.

The action of animal secretions on the polysaccharides has been studied under a wide range of conditions and with many different materials, including blood serum and infusions from various glands and organs of different warm- and cold-blooded animals. In all cases starch, glycogen, and maltose were changed to dextrose. Lactose was not changed by blood serum nor was sucrose. In general, the latter was but little affected. Trehalose was slightly changed in some cases, in others not. Raffinose was unchanged by either blood serum or intestinal juices; α-methyl-glucoside was unchanged but methyl-glucoside was decomposed by an infusion of the intestinal membranes of the horse. Amygdalin was unchanged by the intestinal infusion of ruminants but speedily decomposed by that of other mammals.[6]

Experiments indicate that a sugar not fermentable by a certain organism is still unfermentable when mixed with a second fermentable sugar.[7]

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[1] J. Am. Chem. Soc., **6**, 289.

[2] H. W. Wiley and E. Ewell: *Ibid*, **18**, 428.

[3] E. Beckmann: Ztschr. anal. Chem., **35**, 263; also O. Kunnemann and Hilger: Forsch. Ber. u. Lebensm., etc., **3**, 211.

[4] H. W. Wiley: J. Am. Chem. Soc., **18**, 179.

[5] H. Suringar and B. Tollens: Jour. f. Landw., 1896, 343.

[6] E. Fischer, Sitzungs: Ber., Kgl. Preuss. Akad. d. Wiss., Jan., 1896; also E. Bourquelot and E. Gley: Compt. Rend. Soc. Biol., 1895, 555.

[7] Van Laer: Bull. Assoc. belge. Chimistes, **9**, 319.

By extracting cultures of *aspergillus niger* with water, a soluble ferment is obtained which produces very complete hydrolysis of raffinose, the rotation diminishing from 103° to 50°. An infusion of baker's yeast gave similar results.[1]

Brown and Morris have called attention to an enzyme (cystase) which dissolves cellulose but is rendered inactive at 60°.

Other enzymes are thought to exist which are able to hydrolyze the hemicelluloses, such as arabo-xylan, galacto-araban, etc., but at temperatures below 60°.[2]

A saturated solution of gypsum seems to retard diastatic action temporarily, but, later, saccharification is increased.[3]

W. E. STONE.

PURDUE UNIVERSITY, Feb. 27, 1897.

TRAITÉ ÉLÉMENTAIRE DE MÉCANIQUE CHIMIQUE FONDEE SUR LA THERMODYNAMIQUE. Par P. Duhem, professeur de physique théorique a la faculté des sciences de Bordeaux. Tome I, Principes Fundamentaux de la Thermodynamique, Faux Équilibres et Explosions. Librairie Scientifique, A. Hermann. Paris, 1897. pp. 299.

In order that the contents of this work may be more readily comprehended, the author has prefixed a chapter on the fundamental mathematical conceptions underlying analysis and mechanics. This volume is divided into two books. The first, treating of the *Fundamental Principles of Thermodynamics*, including in part, the doctrine of the conservation of energy, thermochemistry, entropy and thermodynamic potential, the general equations of thermodynamics, perfect gases, stability and isothermic displacement of equilibrium, stability and isentropic displacement of equilibrium, displacement of equilibrium by variation of temperature.

The second has to do with the so-called cases of *False Equilibrium* and with *Explosions*, discussing in four chapters, viscosity and friction, false chemical equilibrium and the point of reaction, the velocity of reactions, and explosions.

As M. Duhem states, this is not an experimental treatise, but chiefly a theoretical and mathematical one. It is, therefore, not a work on physical chemistry as such, in the sense of the *Lehrbuch* of Ostwald, since physical chemistry is, and probably will remain for a long time, primarily an experimental branch of science. Nevertheless, the physical chemist, as well as the mathematical physicist, will find much here of deep interest, and of the highest importance. This is true of the chapters which treat of thermochemistry, and especially of those which deal with the conditions of equilibrium. The unusually clear method of presentation found in the works of Duhem, commends them to all who are interested in that field in which he is so well known. H. C. J.

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[1] E. Bourquelot : J. Pharm. Chim. (6), **3**, 390.

[2] J. Grüss : Wchschr. Brauerei, 1895, 1257.

[3] J. Grüss: Berl. Pharm. Ges., **5**, 258.

ELEKTROCHEMISCHE UEBUNGSAUFGABEN. Für das Praktikum sowie zum Selbstunterricht. Zusammengestellt von Dr. Felix Oettel. Mit 20 Holzschnitten im Texte. Wilhelm Knapp. Halle A. S. 1897. pp. 53.

After discussing the forms of apparatus which are best adapted to obtaining and measuring the current used in effecting electrolytic decompositions, a number of experiments are described. Among these are the electrolysis of hydrochloric acid, the electrolytic precipitations of copper, and the formation of persulphuric acid by the electrolysis of sulphuric acid.

The last, and perhaps the most interesting chapter, is on the decomposition of certain organic substances by the current. The author states in his preface that he owes this chapter to Dr. K. Elbs. It deals with the electrolytic decomposition of sodium acetate into sodium hydroxide, hydrogen, carbon dioxide and ethane; the formation of azobenzene, hydrazobenzene, *p*-amidophenol, or *p*-amidophenolsulphonic acid, by the action of the current on nitrobenzene under different conditions, using different solvents for the nitrobenzene; also the oxidation of paranitrotoluene to paranitrobenzyl alcohol, and the formation of iodoform from a solution containing sodium carbonate, potassium iodide, water, and alcohol. H. C. J.

THEORIE UND PRAXIS DER ANALYTISCHEN ELEKTROLYSE DER METALLE. Von Dr. phil. BERNHARD NEUMANN, Assistant für Hüttenkunde an der Kgl. techn. Hochschule zur Aachen.

The publication of this book is additional evidence that electrolytic methods are rapidly gaining a front rank in analytical chemistry. It is in technical establishments, especially where many analyses are demanded, that these new methods have won due recognition and greatest favor, because of their rapidity, neatness and accuracy.

The purpose of the present volume is to present the practical chemist with those electrolytic methods, which experience has shown to be the best.

It also contains concise, but complete, chapters on the more recent theories of electrolysis, details as to the best sources of electric energy, the measurement and control of the current, and a minute description of the various apparatus used in electrochemical analysis, with directions as to its proper arrangement. Much stress is laid on the important part played by current density in the separation of metals. Indeed, this constitutes a reason in the mind of the author for the preparation and publication of his book.

The chapters relating to the determination of the individual metals, as well as their separation, are quite exhaustive. In this connection it is interesting to note that the author prefers the precipitation of copper from a nitric or sulphuric acid solution, rather than from its double oxalate solution; that zinc is best precipitated from its double cyanide solution, and that the latter solution is also given preference (and rightly) in estimating cadmium, mercury, gold, silver, etc., although the reviewer cannot concur with the statement made on p. 140 that an ammoniacal solution of silver phosphate yields "ungenügende Resultate," for he has frequently observed the contrary. The methods offered for the determination of manganese, while affording good results, are not likely to replace, in iron laboratories at least, the simpler titration methods now in use for this metal.

Under separations the oxalate method is used for copper and iron, notwithstanding "sie giebt nicht immer die gewünschten Resultate." A solution of these metals, containing free sulphuric acid, is best for this purpose, and also for the separation of copper from zinc, manganese, nickel and cobalt, a form of solution first used in 1864 by Gibbs for the separation of copper from nickel.

The author recognizes the fact that double cyanide solutions lend themselves to the successful separation of more metals than any other form of solution, and accordingly recommends them, and describes their proper conditions in detail.

The literature references are numerous. Occasional errors may be detected in them; *e. g.*, *Moore* for *Muhr*, on pp. 130, 151.

However, the little volume is a valuable addition to existing electrochemical works, and its author is entitled to much credit for his labors, as well as for the disinterested but generous consideration of the works of others. E. F. SMITH.

LE FOUR ÉLECTRIQUE. Par M. HENRI MOISSAN, de l'Institut. Paris: G. Steinheil. 1897. 385 pp. Large octavo. Price, 15 francs.

Those who have not followed Prof. Moissan's work for the last five years, would not suspect from the title of this book that it was work of fundamental importance to chemistry. Yet it is this, and more. The work which it chronicles in detail is doubtless the most noteworthy contribution to inorganic chemistry since the discovery of the Periodic Law. The book demands careful study from every chemist; study which is made easy by the beauty and clearness of Moissan's style. It is not possible in a brief review to do more than refer to the chief points of interest, yet a condensed extract from the preface must find place. Moissan says:

"The study of the fluorides of phosphorus led me, after many trials and researches, to the isolation of fluorine. When I had learned to manipulate this element, I thought of utilizing its reactive energy in the reproduction of crystallized carbon. I first showed that two gaseous fluorides of carbon could be easily made, but the pyrogenic decomposition of these gases yielded only lampblack. Though these fluorides did not give the desired result, they led me to take up the systematic study of the three varieties of carbon, and to seek methods of transforming them. Recognizing that pressure was needed to make carbon crystallize, I made use of the increase of volume of cast-iron at the moment of passage from the liquid to the solid state to obtain very high pressure. This reaction occurs at about 1000°, but as I had to dissolve much carbon in the fused iron, I was compelled to heat this metal to a very high temperature. Hence the invention of my electric furnace. I was thus led to construct a laboratory apparatus which can accommodate itself to all conditions of research. I believe it to be simple and convenient. Certainly it has been of great help to me in the reproduction of the diamond, and has also permitted me to extend our knowledge of chemistry at high temperatures. This volume contains the results obtained by use of this apparatus."

The reviewer refuses to mar the eloquence of the last clause of the preface by translation; it must be given in the original.

"Mais ce que je ne puis rendre dans ces chapitres successifs, c'est la joie que j'ai éprouvée à poursuivre toutes ces découvertes. Marcher dans un sillon nouvellement ouvert, se sentir les coudées franches et voir de toutes côtés surgir de nouveaux sugets d'étude, procure un bonheur, que ceux-là seuls, qui ont éprouvé l'âpre plaisir de la recherche peuvent entièrement comprendre."

The book is divided into four chapters. The first treats of the different forms of electric furnace employed; the temperature obtainable is estimated at 3500°. The only reason that this temperature is the limit is that no material known suitable for furnace or crucible can resist this temperature more than a few minutes, and would be instantly destroyed by increased heat. The temperature seems steadily to increase with intensity of current. Then follows a study of the crystallization of metallic oxides, proving that this can be effected by simple heat, which gives a vapor-tension to the fusing oxide favorable to crystallization. For lime the temperature required is about 2000°; for magnesia, higher; copper oxide is dissociated into oxygen and copper; many oxides are studied. An account of fusion and volatilization of refractory substances follows. Substances like magnesium pyrophosphate and asbestos are volatilized with complete dissociation; among many volatilized elements, platinum, uranium, silicon, and carbon may be mentioned. The most refractory oxides are volatilized and dissociated, but under proper conditions, in place of the substances hitherto known to chemists as refractory, new classes of binary compounds are formed which are more or less stable at still higher temperatures. These are the nitrides, borides, silicides, and especially the carbides.

The second chapter is a long and detailed, but fascinating, study of the element carbon in its three chief forms of amorphous carbon, graphite, diamond, and their many sub-forms, tracing the successive polymerization of this element from the simpler polymer in the form of amorphous carbon produced at ordinary temperature and pressure, to the complex polymers formed at high temperatures and pressures as the crystalline graphites or as diamond. This chapter, of course, includes a full description of the successful experiments in reproducing the diamond, which have made Moissan's name so familiar to the public.

The author devotes the third chapter to the preparation of elements in the electric furnace. He prepares chromium, manganese, molybdenum, tungsten, uranium, vanadium, zirconium, titanium, silicium, and aluminium—several for the first time pure—and gives a careful study of the properties and reactions of the single elements, with details of the methods of analysis pursued.

The fourth chapter is a study of the metallic carbides, borides, and silicides. It is impossible in a brief review even to sketch this field, where everything is new. Suffice it to say that Moissan proves that the binary compounds of the metals familiar to us as stable compounds under existing conditions; *i. e.*, the oxides, sulphides, chlorides, etc., cannot exist at high temperatures, but are decomposed, giving place to other binary compounds readily formed under these conditions, and resisting in greater or less degree much higher temperatures without decomposition. In exactly the same sense that copper sulphide is a substituted sulphuretted hydrogen, salt a substituted hydrochloric acid, quick-lime a substituted water, the nitrides are substituted ammonias, the carbides substituted hydrocarbons, the silicides substituted hydrogen silicide, the borides substituted hydrogen boride. Many of these substances indeed yield, by simple contact with water at ordinary temperatures, the hydride from which they are derived. It may suffice to mention as examples the well-known calcium carbide or, more accurately, acetylide, which yields with water pure acetylene and calcium hydroxide; the aluminium carbide or methide, which yields pure methane and aluminium hydroxide:

$$Al_4C_3 + 12H_2O = 3CH_4 + 4Al(OH)_3\ ;$$

lithium nitride, which yields ammonia and lithium hydroxide:

$$NLi_3 + 3H_2O = NH_3 + 3LiOH.$$

Certain of the metallic carbides are not simple substances like these, but when decomposed yield mixtures of different hydrocarbons. On this fact Moissan bases his theory of the origin of natural gas and petroleum. A few pages are given to this theory. Those who are familiar with the theories and the work of Mendeléeff, Engler, and others, on this subject, will perhaps agree with the reviewer in thinking that this previous work harmonizes with and confirms Moissan's theory.

The light which Moissan's work throws on the chemistry of the stars, on the condition of our earth when its temperature was very high, and on the chemical changes which took place when the earth's crust assumed its present condition, must occur to every thoughtful reader, and are briefly discussed by the author.

In conclusion the reviewer would emphatically urge that no teacher should consider himself fitted to instruct in inorganic chemistry to-day, who has not either read this book, or the author's single articles, which have appeared during the last five years in the *Comptes Rendus*, and, in complete form, in the *Annales de Chimie et de Physique* during the years 1895–96.

It is, of course, easier and more profitable to follow the trend of the author's thoughts in the book than in the single articles. Every chemical library should have a copy of this work. Every student reading it will lay it down at the close with the same feeling of admiration for the author's genius and indomitable patience and skill in research, which the reviewer has felt in increasing degree in the study of the single articles during the last five years, and especially on reading this volume.

EDWARD RENOUF.

Correction: Vol. XIX, p. 417. *For* "Lafayette B. Wendel" *read* "Lafayette B. Mendel."